Volume XXIII. *July, 1906.* *Number 1*

THE

PHYSICAL REVIEW.

THE REFLECTION OF CATHODE RAYS FROM THIN METALLIC FILMS.

By S. R. Williams.

Introduction.

CATHODE rays after impingement upon a metallic surface may be considered from three standpoints: (1) Those rays which are reflected, (2) those which are absorbed or give up their charge to the metal, and (3) those which pass through if the metal is in thin enough layers. As to whether the rays reflected or those emerging from the rear side of a thin film are the identical ones which were incident upon the front surface is still an open question.

Among those having investigated the conditions of transmission and the properties of the transmitted cathode ray may be mentioned Hertz,[1] Lenard,[2] Leithaüser[3] and Des Coudres.[4] In a later research Lenard[5] studied the absorption of cathode rays in various media, on which subject Seitz[6] published some results at the same time. To our knowledge of the behavior of the reflected cathode ray, Swinton,[7] Starke[8] and Gehrcke[9] have made valuable contributions.

From these various researches two important conclusions may

[1] H. Hertz, Wied. Ann. 45, p. 28, 1892.
[2] Ph. Lenard, Wied. Ann. 52, p. 27, 1894.
[3] Leithaüser, Ann. d. Physik., 15, p. 283, 1904.
[4] Des Coudres, Physik. Zeitschr., 4, p. 140, 1902.
[5] Ph. Lenard, Ann. d. Physik., 12, p. 714, 1903.
[6] Seitz, Ann. d. Physik., 12, p. 860, 1903.
[7] Swinton, Proc. Roy. Soc., 64, p. 395, 1899.
[8] Starke, Ann. d. Physik., 5, p. 75, 1900.
[9] Gehrcke, Sitzber. d. k. Akad. d. Wissen. zu Berlin, 18, April, 1901.

be drawn: (1) With increasing potential, the transmission of cathode rays through a thin metallic film also increases; (2) the reflection coefficients remain constant for potentials ranging from 4,000 volts upward, if the reflectors are 1 mm. or more thick.

The transmission of cathode rays through thin metallic films shows that the rays penetrate the surface, but when we consider that the reflection coefficients of thick reflectors remain constant for varying potentials, the question arises, does reflection take place at the surface and thus remain constant in amount or do the rays which penetrate the surface suffer reflection from layers in the metal at depths which depend on the potential so that the amount reflected remains unchanged. If all reflection is from the front surface then reflection should be independent of thickness. If however deeper layers are also concerned it might be possible with increasing potential and very thin films to reach a critical point where a part of the rays would pass through and the reflection coefficient of the film be diminished. We might in the later case find for thin films a reflection coefficient diminishing with increasing potential.

To distinguish if possible between these two points of view of cathode ray reflection, the following study was undertaken at the suggestion of Professor E. Warburg and the experiments carried out in the physical laboratory of the University of Berlin.

Methods of Investigation.

From the various researches that have already been made on the reflection and transmission of cathode rays it is evident that there are two methods available for such an investigation: (1) The electrical method in which the charge carried by the reflected rays is measured by a galvanometer. (2) The photometric method in which the fluorescent brightness produced by the reflected rays is taken as a measure of the quantity reflected.

The electric method was first tried and the form of apparatus as used by Starke[1] was adopted in which the charge given up by the absorbed rays was measured instead of the quantity which the reflected rays carry. According to Starke, if a quantity of electricity,

[1] Starke, Ann. d. Physik., 3, p. 97, 100.

Q, transported by cathode rays, falls on a metallic reflector which is connected to earth through a galvanometer, the current which the galvanometer shows is

$$I = Q(1 - r)$$

where r is the reflection coefficient of the metal. Replacing one metal by another whose reflection is r' and the current is

$$I' = Q(1 - r').$$

Q remaining constant in both cases, we can write

$$I/I' = (1 - r)/(1 - r'),$$

whence follows

$$r' = 1 - (1 - r)I'/I. \qquad (1)$$

Thus if r' be the reflection coefficient of a thin film and r that of a plate of the same metal, then any variation in r' would cause a change in I' by which if r was known r' could be determined. Here I' must include transmitted as well as absorbed charges.

In this way the reflection coefficient of a thin aluminum film about 1.5 μ was compared with an aluminum reflector, about 2 mm. thick, for the amount of cathode rays which they reflected. The reflection coefficient of the thick reflector was taken as 25 per cent., the value found by Austin and Starke.[1] Although comparisons were made at potentials as high as 18,000 volts no variations between the two currents I and I' could be detected. A d'Arsonval galvanometer with 10,000 ohms resistance being used to measure the currents. As higher potentials with the tube used gave inconstant readings, the results by the electrical method were in this case negative. These negative results however did not seem to be conclusive evidence. Since aluminum reflects 25 per cent., the other 75 per cent. given up to the reflector is measured by the galvanometer, hence a fairly large percentage variation in the amount reflected would have to occur before the variation would appreciably affect the galvanometer reading. Moreover this method offered no means of studying the loss in velocity of the rays reflected from thin films, which would be of especial interest here if any change in the amount reflected occurred.

[1] Austin u. Starke, Ann. d. Physik., 9, p. 292, 1902.

On those grounds the electrical method was given up and the photometric method tried since it seemed to offer as great a sensibility and had the advantage that it was possible also to investigate the loss in velocity of rays reflected from thin films.

When cathode rays fall upon a fluorescent screen, the brightness of the illumination, H, will depend on the current density of the rays per unit area which falls on the screen, and some function of the potential under which the rays are produced, such as $H \equiv [I \times f(V)]$, where I represents the current density and V the potential. This dependence of the brightness of fluorescence on the current density and the potential under which they are produced has been carefully worked out by Leithaüser.[1] From his data it appears that the brightness is approximately proportional to the current density of the rays falling upon the screen, while on the other hand, the dependence of brightness on the potential with constant current shows that this relation is not a linear function, but that the ratio $\frac{\text{Brightness}}{\text{Discharge Potential}}$ at first increases with increasing potential while at still higher potentials, the ratio again decreases. Hence when comparing two fluorescent spots produced by cathode rays, the discharge potential must be taken into account. From these relations worked out by Leithaüser, we can compare the current densities of cathode rays from any two sources, by knowing the relative brightness of the fluorescence produced when they impinge upon a screen, for

$$\frac{H}{H'} = \frac{(I)f(V)}{(I')f(V')},$$

thus $H/H' = w$, a ratio which may be determined by means of a photometer. From these quantities we then have

$$\frac{I}{I'} = w\frac{f(V')}{f(V)} \qquad (2)$$

where the ratio $f(V')/f(V)$ may be obtained from Leithaüser's tables.

The two sources of cathode rays just mentioned may be two reflectors, one of which is a thin aluminum film, whose reflection coefficient is to be investigated, the other being a thick aluminum reflector, whose reflection coefficient is known.

[1] Leithaüser, Ann. d. Physik., 15, p. 283, 1904.

If then rays of the same intensity fall on both reflectors, by the equation just given, we can determine the ratio of the quantities reflected, by knowing the ratio of brightness of the fluorescence and by the data given in the tables of Leithaüser. By allowing the rays reflected from these two sources to pass through narrow apertures, side by side, narrow and sharply defined fluorescent spots may be obtained on the screen, which, by means of a magnetic field, can be drawn out into magnetic spectra, parallel to each other, and comparison of the amounts reflected be made.

The final form of the apparatus as used is shown in Fig. 1. In general the apparatus resembled that used by Gehrcke,[1] only with changes to suit the present problem. The most noteworthy difference is that Gehrcke studied the reflected rays which had struck the reflector at an angle of 45°, in this work the rays were incident normally upon the reflectors.

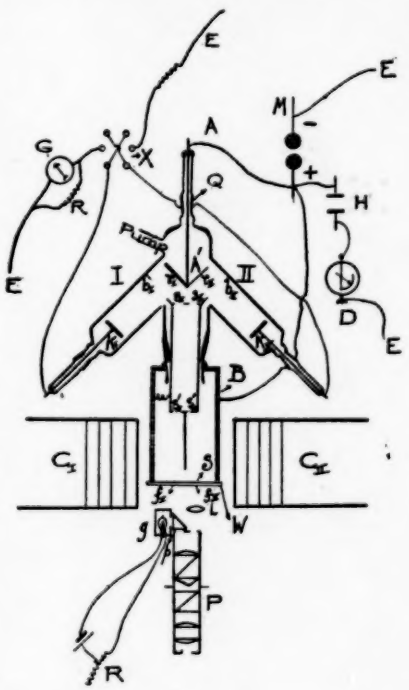

Fig. 1.

The apparatus consisted of a bronze box, *B*, 19 cm. high, 6 cm. broad and 13 cm. in depth, which allowed for space in which the rays might be drawn out into parallel spectra. The rear side of the box was closed by means of a thick piece of plate glass, *W*. This plate carried the fluorescent screen which was made by sprinkling calcium sulphide on the thinnest possible layer of grease, rubbed over the inner surface of the glass plate. The advantage of the calcium sulphide as a fluorescent substance is, that the fluorescent after-glow dies away rapidly after the bombardment of the cathode

[1] Gehrcke, Sitzber. d. k. Akad. d. Wissen. z. Berlin, 18, April, 1904.

particles has ceased, allowing measurements to be made in rapid succession on the same part of the screen. This property varies with the sample. Into a circular opening in the front side of the box, B, was sealed the discharge tube, which consisted of a main tube, 4 cm. in diameter, to which were joined two equal side tubes, I and II, 3 cm. in diameter, entering the main tube at an angle of 45°. These side tubes contained the cathodes K_I and K_{II}, the faces of which were parallel to the reflectors, r_I and r_{II}, and at a distance of about 8 cm. from them.

For the production of the discharge current a 20-plate influence machine, M, of the Toepler type, was used. Its negative pole was earthed, while the positive pole was connected to the anode, A. The rod on which the reflectors, r_I and r_{II}, were fixed, served as anode and since the metal cylinder containing the slits, s_I, s_{II}, s_I' and s_{II}', and the screens, b_I and b_{II}, were within about 2 cm. of the reflectors, they were charged to the same potential as the reflectors, by metallic connection with the side of the box, B, and positive pole of the machine as shown. To work with high potentials, the box, B, was insulated on heavy glass plate to prevent leakage to earth through platform on which the apparatus was placed. The cathodes, K_I and K_{II}, were then earthed to complete the circuit. The potential at the cathodes being almost zero, allowed the measuring of the cathode discharge with a galvanometer, G, without the disturbing influences of static charges under high potentials. The two cathodes were connected to a six-pole reversing switch, X, in such a way that first one cathode and then the other could be connected to earth through the shunted galvanometer, G, while simultaneously the other cathode was earthed through a resistance, R, equal to the resistance of the shunted galvanometer. If the current was the same in both side tubes, then the deflection of the galvanometer should be the same in both cases, a condition obtained in all final readings. Thus cathode rays passing out from the two cathodes, K_I and K_{II}, fall on the reflectors, r_I and r_{II}, respectively after having passed through horizontal slits 1 by 15 mm. in the screens, b_I and b_{II}. From the two reflectors the rays are reflected diffusely in all directions and part of the rays from r_I pass through the two horizontal slits, s_I and s_I' (1 by 6 mm. in size and in the same plane as

the slit in b_I), and finally fall upon the fluorescent screen, S, producing the fluorescent spot, f_I. Similarly the rays from r_{II} produce the fluorescent spot, f_{II}. f_I and f_{II} are then drawn out into magnetic spectra by means of the solenoids, C_I and C_{II},[1] and the spectral distribution of the rays measured.

It is at once apparent that this method will not give correct results unless the intensities of cathode discharge from K_I and K_{II} are equal. The elimination of such inequalities from the preliminary measurements was the cause of so much trouble that it may be useful to mention the precautions finally taken to prevent errors of this sort.

As may be seen from Fig. 1 the apparatus is symmetrical about an axis running through the anode, A, and the photometer, P. In putting the apparatus together, unless each part was symmetrically placed, inequality of the two currents in the side tubes occurred. Also when the two reflectors, r_I and r_{II}, were of different metals, the currents were not the same. This was to be expected, as the reflector having the largest reflection coefficient produced a greater ionization in the discharge space and so more current passed through the side-tube which carried the reflector of largest reflection coefficient. In comparing copper and aluminum, for example, the reflection coefficient of copper is 45 per cent. and that of aluminum 25 per cent., a larger current always passed through the side-tube facing the copper reflector. This error was eliminated by placing between the cathodes and the reflectors the screens, b_I' and b_{II}, with narrow slits in them which prevented rays from the reflectors being thrown back into the discharge space to any appreciable amount.

An inequality of cathode discharge in the two branch tubes due to unavoidable dissymmetry of construction was still present and to eliminate this from the results the two reflectors, r_I and r_{II}, were mounted on a shaft, A', which could be rotated by means of the ground-glass joint, Q, through which the shaft passed. Any inequality of cathode discharge in either one of the branches could be eliminated by taking readings from both branches with the mirrors in one position and repeating with the mirrors reversed. This gave a mean which was free from errors of this sort. Any in-

[1] S. Simon, Wied. Ann., 69, p. 595, 1899.

equalities of size or position of the slits, or lack of uniformity in the fluorescent screen was also eliminated at the same time, as measurements were made of each reflector under exactly the same conditions as the other. A further inspection of the symmetry of the apparatus shows that the fluorescent spots, f_I and f_{II}, could be compared directly with each other by means of the photometer [1] or by inserting a right-angled prism, p, over one opening of the photometer the brightness of either spectrum could be compared with the constant brightness of an incandescent lamp. The direct comparison of the two spots, f_I and f_{II}, worked very well until high potentials were reached and then discharge would take place first through one side-tube and then the other in quick succession. For high potentials only one cathode was used and first one reflector and then the other was turned into position and the brightness of the spectra compared with the standard lamp, the current being held constant as shown by the galvanometer during the rotation of the reflectors.

A Sprengel pump was used in exhausting the tube. As soon as an adequate vacuum was reached the pump was cut off and the occluded gases, driven from the cathodes by the discharge, were absorbed by cocoanut shell charcoal in a bath of liquid air according to Dewar's method.[2] This gave most satisfactory and constant results. By varying the opening between the tube and the receptacle holding the charcoal almost any pressure could be maintained for some considerable time, so that with the influence machine giving constant current very steady conditions were obtained.

The spectra formed on the fluorescent screen, when a magnetic field was produced, were focused by means of a lens, L, on the openings of the photometer, the image being natural size. By means of a faintly illuminated scale, the amount of deflection and dispersion, and the position of the photometer openings in the spectra were easily and quickly determined. Only those readings were accepted in which constant current conditions were maintained.

For convenience of observation, the length of spectra were divided into four regions and for each of the four positions of the photometer ten readings were made, during which both current and

[1] F. F. Martens, Phys. Zeitschr., 1, p. 299, 1900.
[2] J. Dewar, Compt. Rendus, 139, p. 261, 1904.

potential were held constant. The fourth region was generally too faint in illumination to be measured. Thus sixty readings were necessary to determine one reflection coefficient for a single potential, as the two spectra had to be separately compared, region by region, with the standard lamp. On repcating such a set of readings it was found that from 6 to 7 per cent. accuracy could be obtained.

Having the apparatus to all appearances free from errors it was of interest to compare this method with the electrical method used by Starke.[1] Accordingly a comparison of the reflection coefficients of copper and aluminum was made. The reflection coefficients of these two metals Starke determined by direct methods and afterwards verified his results by a comparative method, hence their values were pretty well fixed.

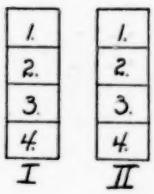

Fig. 2.

If we divide the two magnetic spectra to be compared into sections as shown in Fig. 2, by knowing the ratio of the brightness of the various sections we can determine the relative current densities of cathode rays producing the spectra, from the equation,

$$\frac{I_I}{I_{II}} = \frac{n_1 + n_2 k_1 + n_3 k_2 + n_4 k_3}{1 + k_1 + k_2 + k_3} + \cdots \qquad (3)$$

where the n's represent the ratios of brightness between sections having the same deflection, here indicated by sections having the same number. These ratios are read directly from the photometer as we are comparing cathode rays of the same potential and the brightness in such a case Leithaüser has shown is directly proportional to the current density of rays producing the fluorescence. The k's are ratios of the intensities of the cathode rays between 1 and 2, 1 and 3, 1 and 4, etc., determined by equation (2). The k's were always measured in the brightest spectrum which in this case was that of copper. If

$$n_1 = n_2 = n_3 = n_4$$

then the distribution throughout the two spectra is the same and

[1] Starke, l. c.

$$I_I/I_{II} = n.$$

This means that the ratio of brightness of the two undeflected spots for the condition of equal distribution in the two spectra is the same as the ratio of the reflection coefficients.

The undeflected spots, f_I and f_{II}, were 5 mm. wide and somewhat longer and when the magnetic field was on, these were drawn out into spectra a little over 15 mm. long. The width of the photometer openings were also 5 mm. so that lengthwise of the spectra there were three sections 5 mm. wide that could be measured. Increasing the magnetic field lengthened the spectra but decreased the brightness, so that a spectrum 18 to 20 mm. in length was found the most advantageous in use.

The distance from the centers of the undeflected spots to the centers of the various sections was taken as the deflection of that section. The potential of section 1, was taken as the potential at which the rays were produced since rays which come direct from cathode without reflection would be deflected by this amount as shown by Gehrcke.[1] Of course with such wide photometer openings as those used in the present work the rays producing the fluorescence on the two sides of the opening would of course correspond to different potentials, but by considering the brightness observed in each region as that belonging to the center, we get a fair average, although not an absolute value. Any such error was still further reduced when two equally deflected sections of neighboring spectra were compared.

In a magnetic spectrum the deflection, z, varies inversely as the velocity of the rays, v. But the velocities stand in the same ratio as the square roots of the potentials, so that we may write $z^2 \propto 1/V$. For the various sections of the spectra, z, could be measured, and the potential and deflection of section 1 being known, the corresponding potential for the others could be determined.

Since the reflection coefficients of massive metal plates remain constant for varying potentials, to compare the coefficients of aluminum and copper, a potential of 16,500 volts was chosen, as at this potential a very steady current could be maintained. The

[1] Gehrcke, Sitzber. d. k. Akad. d. Wissen. z. Berlin, 18, April, 1901.

data obtained in this photometric comparison are given herewith and graphically shown in Fig. 3, where the current densities are plotted as ordinates, and abscissas as distances from center of section 1, z_0 being the magnetic deflection of section 1.

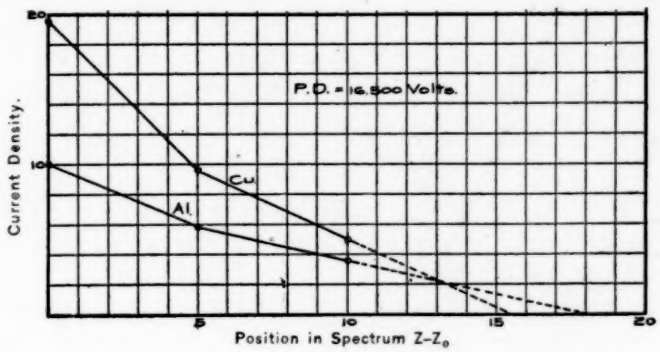

Fig. 3.

Deflection of section	(1) 1.7 cm.	(2) 2.2 cm.	(3) 2.7 cm.
Voltage " "	(1) 16,500	(2) 9,850	(3) 6,550
Corresponding brightness	(1) 182.6	(2) 110.1	(3) 56.4
(Interpolated from the tables of Leithaüser.)[1]			
Measured brightness	(1) 0.601	(2) 0.178	(3) 0.044

$1_{al}/1_{cu} = n_1 = 0.518.$ $2_{al}/2_{cu} = n_2 = 0.616.$ $3_{al}/3_{cu} = n_3 = 0.787.$

(These ratios were also photometrically measured.)

$$\frac{0.178}{0.601} \times \frac{182.6}{110.1} = k_1 = 0.491, \quad \frac{0.044}{0.601} \times \frac{182.6}{56.4} = k_2 = 0.337.$$

$$\frac{I_I}{I_{II}} = \frac{n_1 + n_2 k_1 + n_3 k_2}{1 + k_1 + k_2} = \frac{0.518 + (0.616 \times 0.491) + (0.787 \times 0.237)}{1 + 0.491 + 0.237}$$

$$= \frac{1.006}{1.728} = 0.58,$$

the ratio of the reflection coefficients of aluminum and copper. Austin and Starke[2] found as the value for this ratio, 0.56 which, considering the accuracy of 6 to 7 per cent. which this method afforded, is a fair agreement. The results showed that the apparatus was in working order and free from large errors. The copper reflector was replaced in succession by a series of thin aluminum

[1] Leithaüser, Ann. d. Physik., 15, p. 296, 1904.

[2] Austin u. Starke, Ann. d. Physik., 9, p. 292, 1902.

films and the properties of the rays reflected from them compared with the reflection from a thick aluminum plate. The first film used was 0.53 μ thick, the thickness being measured with a Zeiss Dickenmesser. Ten and twenty thicknesses of the aluminum leaf were laid together and the total thickness divided by the number gave results agreeing to 0.01 μ. The thickness was not over 0.53 μ although it might possibly have been thinner as some allowance must be made for the air layers between the leaves. This error was made as small as possible however by pressing the films firmly together in measuring.

On comparing the brightness of fluorescence produced by the rays reflected from a thin and a thick aluminum reflector at higher potentials, viz., about 20,000 volts, the difference was so great as to be readily observed with the naked eye.

Since the reflection coefficient of the films varied for potentials above a critical potential, it was necessary to measure the entire spectrum for each potential used. The first film was measured at the potentials 11,000, 16,500, 21,800 and 27,750 volts. For these high potentials it was necessary to connect a condenser in series with the Braun electrometer, D, as shown in Fig. 1, as the range of the electrometer, was from 4,000 to 10,000 volts only. This worked satisfactorily as long as the atmosphere in the room was dry. If it was not, whenever the influence machine was short-circuited, a charge would remain on the electrometer due to leakage over the glass supports.

The observations were made in the same order as in the comparison of aluminum and copper already described and the results are given in the following tables and curves:

Potential = 11,000 volts.			
Deflection of section	(1) 2.3 cm.	(2) 2.8 cm.	(3) 3.3 cm.
Voltage of section	(1) 11,000	(2) 7,400	(3) 5,350
Corresponding brightness	(1) 129.0	(2) 66.6	(3) 43.6
Measured brightness	(1) 1.83	(2) 0.478	(3) 0.197

$$n_1 = 1.021, \quad n_2 = 0.958, \quad n_3 = 0.949.$$

$$\frac{0.478}{1.83} \times \frac{129.0}{66.6} = k_1 = 0.505.$$

$$\frac{0.197}{1.83} \times \frac{129.0}{43.6} = k_2 = 0.318.$$

I_I = total quantity in spectrum from thin film.

I_{II} = total quantity in spectrum from thick film.

$$\frac{I_I}{I_{II}} = \frac{n_1 + n_2 k_1 + n_3 k_2}{1 + k + k_2} = \frac{1.021 + (0.958 \times 0.505) + (0.949 \times 0.318)}{1 + 0.505 + 0.318}$$

$$= \frac{1.807}{1.823} = 0.991 = \frac{x}{25},$$

where 25 per cent. is the amount reflected by the thick reflector. That is, 0.991 is the ratio of the reflection coefficients of the thin

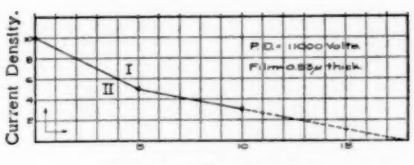

Fig. 4.

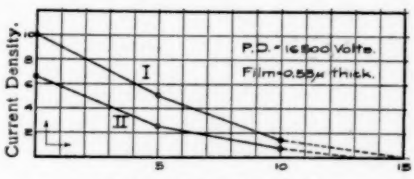

Fig. 5.

and thick aluminum reflectors at a potential of 11,000 volts. This means that within the accuracy of the method the two reflectors are equal. (See Fig. 4.)

Potential = 16,500 volts.			
Deflection of section	(1) 2 cm.	(2) 2.5 cm.	(3) 3 cm.
Voltage of section	(1) 16,500	(2) 10,550	(3) 7,350
Corresponding brightness	(1) 182.6	(2) 122.2	(3) 66.0
Measured brightness	(1) 2.65	(2) 0.868	(3) 0.130

$$n_1 = 0.656, \quad n_2 = 0.517, \quad n_3 = 0.451.$$

$$\frac{0.868}{2.65} \times \frac{182.6}{122.2} = k_1 = 0.489.$$

$$\frac{0.130}{2.65} \times \frac{182.6}{66.0} = k_2 = 0.135.$$

$$\frac{I_I}{I_{II}} = \frac{0.656 + (0.517 \times 0.489) + (0.451 \times 0.135)}{1 + 0.489 + 0.135}$$

$$= \frac{0.970}{1.624} = 0.597 = \frac{x}{25}.$$

$x = 14.9$ per cent. reflected at a potential of 16,500 volts. (See Fig. 5.)

Potential = 21,800 volts.			
Deflection of section	(1) 1.8 cm.	(2) 2.3 cm.	(3) 2.8 cm.
Voltage of section	(1) 21,800	(2) 13,350	(3) 9,000
Corresponding brightness	(1) 195.0	(2) 161.5	(3) 95.8
Measured brightness	(1) 3.57	(2) 0.98	(3) 0.25

$$n_1 = 0.518, \quad n_2 = 0.274, \quad n_3 = 0.216.$$

$$\frac{0.98}{3.57} \times \frac{195.0}{161.5} = k_1 = 0.331.$$

$$\frac{0.25}{3.57} \times \frac{195.0}{95.8} = k_2 = 0.142.$$

$$\frac{I_I}{I_{II}} = \frac{0.518 + (0.274 \times 0.331) + (0.216 \times 0.142)}{1 + 0.331 + 0.142}$$

$$= \frac{0.640}{1.473} = 0.434 = \frac{x}{25}.$$

$x = 10.8$ per cent. reflected from the thin reflector at a potential of 21,800 volts. (See Fig. 6.)

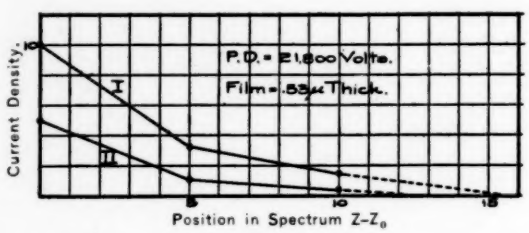

Fig. 6.

Potential = 27,750 volts.

Section (3) of the spectrum from the thick reflector was so faint in intensity that no measurements could be taken, as were also (2) and (3) of the spectrum from thin film.

Deflection of section	(1) 1.5 cm.	(2) 2 cm.
Voltage of section	(1) 27,750	(2) 15,600
Corresponding brightness	(1) 225.5	(2) 179.4
Measured brightness	(1) 3.06	(2) 0.239

$$n_1 = 0.329.$$

$$\frac{0.239}{3.06} \times \frac{225.5}{179.4} = k_1 = 0.096.$$

$$\frac{I_I}{I_{II}} = n_1 = 0.329 = \frac{x}{25}.$$

$x = 8.22$ per cent. reflected at the potential of 27,750 volts from a thin film. (See Fig. 7.) From the above results the reflection coefficients of an aluminum film, $0.53\,\mu$, may be plotted as a function of the potential. (See Fig. 12.)

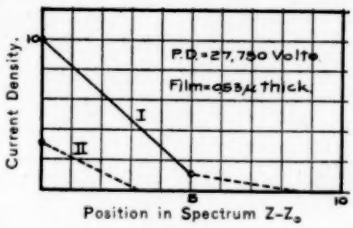

Fig. 7.

Next the reflection of an aluminum film, $1.90\,\mu$, was measured as described above. The results follow:

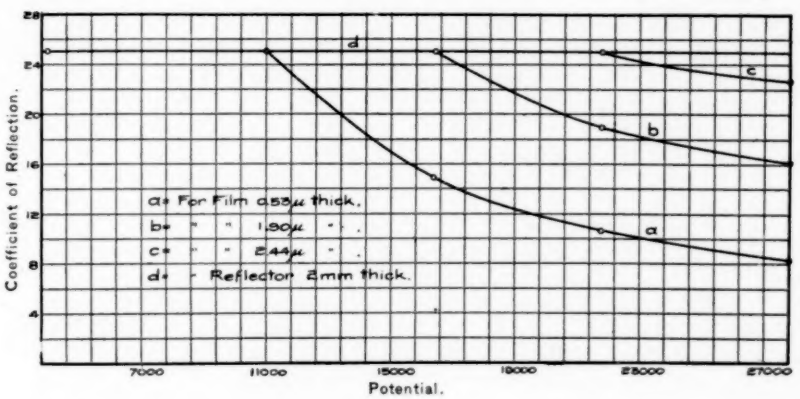

Fig. 12.

Potential = 16,500 volts.			
Deflection of section	(1) 2.1 cm.	(2) 2.6 cm.	(3) 3.1 cm.
Voltage of section	(1) 16,500	(2) 10,750	(3) 7,600
Corresponding brightness	(1) 182.6	(2) 125.2	(3) 69.7
Measured brightness	(1) 2.99	(2) 0.736	(3) 0.245

$$n_1 = 1.023, \quad n_2 = 0.978, \quad n_3 = 0.934.$$

$$\frac{0.736}{2.99} \times \frac{182.6}{125.2} = k_1 = 0.358.$$

$$\frac{0.245}{2.99} \times \frac{182.6}{69.7} = k_2 = 0.214.$$

$$\frac{I_I}{I_{II}} = \frac{1.023 + (0.978 \times 0.358) + (0.934 \times 0.214)}{1.572}$$

$$= \frac{1.572}{1.572} = 1.00 = \frac{x}{25}.$$

$x = 25$ per cent. reflected from film $1.9\,\mu$ thick at a potential of 16,500 volts. The reflection is the same as a thick reflector. (See Fig. 8.)

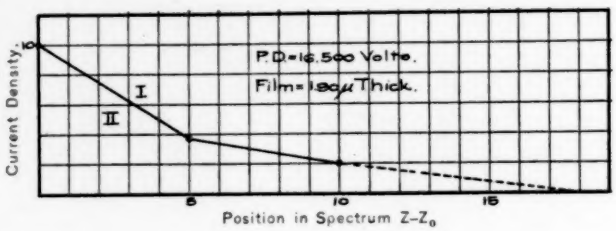

Fig. 8.

Potential = 21,800 volts.			
Deflection of section	(1) 1.8 cm.	(2) 2.3 cm.	(3) 2.8 cm.
Voltage of section	(1) 21,800	(2) 13,350	(3) 9,000
Corresponding brightness	(1) 195.0	(2) 161.5	(3) 95.8
Measured brightness	(1) 4.58	(2) 0.574	(3) 0.225

$$n_1 = 0.796, \quad n_2 = 0.710, \quad n_3 = 0.555.$$

$$\frac{0.574}{4.58} \times \frac{195.0}{161.5} = k_1 = 0.151.$$

$$\frac{0.225}{4.58} \times \frac{195.0}{95.8} = k_2 = 0.099.$$

$$\frac{I_I}{I_{II}} = \frac{0.796 + (0.710 \times 0.151) + (0.555 \times 0.099)}{1.250}$$

$$= \frac{0.958}{1.250} = 0.767 = \frac{x}{25}.$$

$x = 19.2$ per cent. reflected at potential of 21,800 volts. (See Fig. 9.)

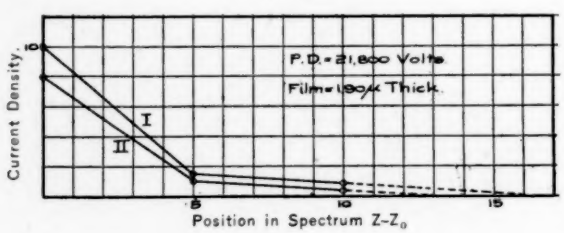

Fig. 9.

Potential = 27,750 volts.		
Deflection of section	(1) 1.5 cm.	(2) 2.0 cm.
Voltage of section	(1) 27,750	(2) 15,600
Corresponding brightness	(1) 225.5	(2) 179.4
Measured brightness	(1) 4.41	(2) 0.441

$$n_1 = 0.671, \quad n_2 = 0.510.$$

$$\frac{0.441}{4.41} \times \frac{225.5}{179.4} = k_1 = 0.125.$$

$$\frac{I_I}{I_{II}} = \frac{0.671 + (0.510 \times 0.125)}{1.125} = \frac{0.735}{1.125} = 0.653 = \frac{x}{25}.$$

$x = 16.3$ per cent. reflected at this potential of 27,750 volts. (See Fig. 10.) Just as for the previous film, so here we can plot the reflection coefficients as a function of the potential. (See Fig. 12.)

Finally the reflection of an aluminum film 2.44 μ thick was compared with a massive plate for potentials of 21,800 and 27,750 volts. At the lower potential, plate and film reflected equally. The results for 27,750 volts follow :

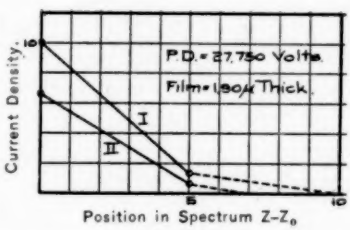

Fig. 10.

Deflection of section	(1) 1.5 cm.	(2) 2.0 cm.
Voltage of section	(1) 27,750	(2) 15,600
Corresponding brightness	(1) 225.5	(2) 179.4
Measured brightness	(1) 3.61	(2) 0.640

$$n_1 = 0.947, \quad n_2 = 0.756.$$

$$\frac{0.640}{3.61} \times \frac{225.5}{179.4} = k_1 = 0.222.$$

$$\frac{I_I}{I_{II}} = \frac{0.947 + (0.756 \times 0.222)}{1.222} = \frac{1.114}{1.222} = 0.911 = \frac{x}{25}.$$

$x = 22.7$ per cent. reflected from a film 2.44 μ thick at a potential of 27,750 volts. (See Fig. 11.) For the curve of reflections plotted as a function of the potential, see Fig. 12.

Having thus found a variation of reflection with thickness for

aluminum, it seemed of interest to measure the reflection coefficients of thin films of other metals. In place of the aluminum reflectors a thick copper reflector and a copper film 0.66 μ thick were compared. For the highest potential, viz., 27,750 volts no difference in reflection was found. Since the gradient of brightness in a

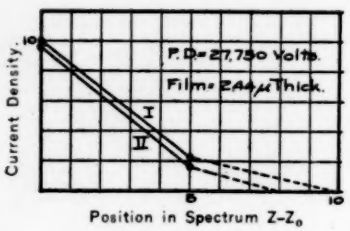

Fig. 11.

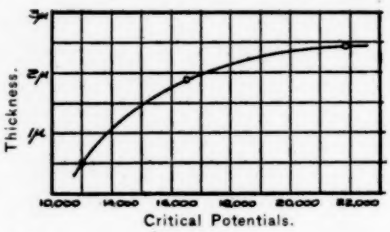

Fig. 13.

spectrum reflected from copper is large as compared with aluminum, the spectra were so short that measurements could only be made in the first section, so that

$$\frac{I_I}{I_{II}} = 1.002 = \frac{x}{45}, \quad x = 45.0$$

for a copper film 0.66 μ thick and at a potential of 27,750 volts. Thus there is a marked difference in behavior of thin aluminum and thin copper films.

If we plot as shown in Fig. 13 the thickness of aluminum films used, as a function of the potential at which the reflection begins to diminish we find that the curve rises quite rapidly to a point between 1.90 μ and 2.44 μ and then becomes more nearly parallel to the axis of abscissas. It thus appears that for reflectors 1 mm. thick it would take an infinite potential before any of the reflected rays would be lost by transmission. In other words this would be saying that whatever the potential, the reflected rays are never from a depth greater than 1 mm.

DISCUSSION OF RESULTS.

From the data just given, we are in a position to discuss some of the conditions under which the reflection of cathode rays take place, especially when reflected from thin films.

The question as to whether the reflection of cathode rays from metals occurs at the surface or whether there is penetration and then reflection has been answered by the results in such a way as to leave no doubt but what the rays penetrate to various depths, depending on the potential, and are then reflected. In the beginning it was assumed that a part of the cathode rays, which would be reflected from a thick film, would in the case of a thin one be lost by transmission after a critical potential was reached and so a thin film would not show as large a reflection as a thick one. The results substantiate this view in that a difference in the quantities reflected, depending on thickness and potential, was found. This dependence of reflection upon potential and thickness will here be discussed more in detail.

For the film 0.56 thick at a potential of 11,000 volts the reflection coefficients of the thin and the thick reflectors are the same. At 11,000 volts then the critical potential has not been reached. On increasing the potential however, a difference occurs, and the only way the decrease in the amount reflected from the thin film can be accounted for is that a part has been lost by transmission. This indicates then that the reflection is not all taking place at the surface of the reflectors, but that there is penetration and then reflection for some of the rays. Although at 11,000 volts the thin film did reflect as much as a thick one, this is not saying that none of the cathode rays passed through the thin film, for behind the film a fluorescence on the walls of the tube showed that some of the rays were coming through, thus some rays penetrate even farther than those reflected from the greatest depths. At the same potential, viz., 11,000 volts, and with a film 1.8 μ thick, Leithaüser [1] still found some transmission.

Again the data and the curves show that there is a decrease in the quantity of rays reflected as one goes from rays of less to those of greater deflection in the magnetic spectrum, further the difference in brightness of corresponding sections of the two spectra is greatest in the most deflected portions, *i. e.*, from equation (3) $n_3 < n_2 < n_1$. This is in accord with what has just been said concerning the reflection of rays which have penetrated to greater depths and which

[1] Leithaüser, Ann. d. Physik., 15, p. 305, 1904.

have been slowed down in consequence. Take a case where a difference in reflection from the two reflectors occurs. Those rays which are penetrating farther into the thick film than the thickness of the thin one are being thrown out and form a large part of the most deflected portion of the spectrum. Consequently the difference in brightness of the most deflected portion of the two spectra will be greater than in the less deflected part, because in the case of the thin film the larger part of those rays which form the most deflected part of spectrum have been lost by transmission, and so we find there the greatest difference in brightness between the two spectra. Fig. 11 illustrates the point in question. The difference in brightness of the least deflected portions of the two spectra is so small that it might pass as an error in the reading. In the next section of the two spectra however a much larger difference occurs, showing that for that part of spectrum from the thin film, a part of the rays has been lost by transmission.

The penetration of cathode rays into copper is interestingly shown by the results given on page 18 where a thin and a thick copper reflector are compared. Here the penetration of the reflected rays is very much less than in aluminum. For a potential of 27,750 volts the penetration of the reflected rays in copper must be less than 0.66 μ as this thickness reflected as much as a plate 2 mm. thick. With an aluminum film and the same potential, viz., 27,750 volts, the penetration of the reflected rays was about 2.5 μ as curve 9 shows. Fig. 3 and the results given in the comparison of the amounts reflected from thick reflectors of aluminum and copper, show that the reflection, in the case of copper must take place nearer the surface of the reflector as the difference in brightness between corresponding sections of the spectra measured was greatest in the least deflected portions, for $n_1 < n_2 < n_3$, that is, the larger part of the rays from the copper reflector were being reflected without appreciable loss of velocity. The spectrum from the copper reflector was also noticeably shorter in length than the one from aluminum. As one approached the more deflected portions of the spectra therefore, the ratio between the brightnesses approached unity. The values given also indicate this, viz.,

$$n_1 = 0.518, \quad < n_2 = 0.616 < n_3 = 0.787.$$

That Gehrcke[1] did not find so great a difference in the spectra of the rays reflected from copper and aluminum is quite likely due to the fact that he was not using normal incidence of the rays in his work.

Sufficiently thin films of other metals with known reflection coefficients could not be obtained, but from the data given above for copper and aluminum, and the fact that Starke[2] found an increasing reflection coefficient the greater the density of the metal, would lead one to infer that the denser the material of the reflector, the less the penetration of the reflected rays.

Summary of Results.

1. The reflection of cathode rays does not all take place at the surface of a metal, but there is penetration and then reflection for a large part of the reflected rays.

2. From a critical potential on, a thin metallic film of aluminum reflects less than a thick one since a part of the rays have been lost by transmission.

3. This decrease in the amount reflected from a thin film appears first in the most deflected rays and with increasing potential will also be found in the least deflected portion.

4. The critical potential depends on the thickness and the nature of the film. For aluminum this critical potential for thicknesses $0.56\,\mu$, $1.90\,\mu$ and $2.44\,\mu$ is 11,000, 16,500 and 21,800 volts respectively. For a copper film of thickness $0.66\,\mu$, the critical potential has a value greater than 27,750 volts.

5. The foregoing data has shown a fair qualitative agreement with the theory deduced by Professor E. Warburg,[3] although the values given do not show the desired agreement with those calculated.

In conclusion the writer takes pleasure in acknowledging his indebtedness to Professor E. Warburg, under whose direction the foregoing work was undertaken, for many kindnesses and helpful suggestions throughout the course of the experiments.

[1] Gehrcke, l. c.

[2] Starke, l. c.

[3] Theories on the reflection of cathode rays have been given by Professor E. Warburg, Verhandl. d. Deut. Physik. Gesell., VI. Jahrg., Nr. 1; J. Stark, Phys. Zeitschrift, 3, p. 161, 1901; J. J. Thomson, Conduc. of Elec. Through Gases, p. 509.

ON THE PHYSICAL PROPERTIES OF FUSED MAGNESIUM OXIDE.

BY H. M. GOODWIN AND R. D. MAILEY.

IN connection with a recent note from the Königlichen Porzellan Manufaktur[1] on the manufacture of tubes, crucibles, etc., of pure oxide of magnesium, we have thought that the results of various experiments which we have recently made on the physical properties of this substance after it has been actually fused, may prove of some interest.

Our attention was first directed to the preparation of fused oxide of magnesium in an attempt to find a substance which at temperatures up to at least 1000° C. would serve as suitable containing vessels for fused salts in an investigation now in progress on their electrical conductivity, *i. e.*, a substance which would possess the properties of being chemically inert, a nonconductor of electricity, and having a sufficiently high melting point to retain its shape at the temperatures mentioned. A small coefficient of expanson was also desired. We were particularly desirous of obtaining tubes or rods of such a substance. Whether the material described by the Charlottenburg firm is magnesia which has actually been fused or not is not quite clear. It seems highly improbable, however, that tubes of the fused material 80 cm. long and 7 cm. in diameter and crucibles 50 cm. high and of any diameter have been made. These are probably moulded under pressure from powdered magnesia and then heated to a high temperature.

After experimenting with a number of silcates and metallic oxides, both in the natural crystalline form and artificially prepared, in the hopes of finding a satisfactory material, it was decided to try to make pure fused magnesium oxide. That this should be possible in the electric furnace seemed probable, as Moissan states that the carbide is not formed when the oxide is heated with carbon. The

[1] Zeitschrift für Electrochemie, *11*, 581, 1905.

first attempt was made in a graphite-resistance furnace. A pure Acheson graphite rod, 18 inches long and ¾ inch outside diameter, was bored with a ½-inch drill and the ends fixed into large graphite block terminals for leading in and out the current. The furnace was mounted vertically, packed with coke to prevent excessive oxidation of the graphite tube and the whole heat-insulated with fire brick. The furnace was heated by current from a 50 kw. transformer, the voltage of which could be varied by steps of 10 volts from 160 volts to 10 volts. From 20–30 kw. were used in the furnace to maintain the temperature required. Chemically pure magnesium oxide was fed in at the top of the furnace in the form of powder and packed down by means of a graphite rod. In this way it could be melted and rods of the fused oxide were obtained about one fourth inch in diameter and two inches long.

In no case, however, could rods be formed as large as the interior diameter of the bored graphite rod, owing to an action between the oxide and either of the walls of the tube, or gases given off from or diffusing through the walls of the enclosing tube. This was indicated by the formation of a volatile product which condensed to a black mass in the upper cooler portions of the furnace. To prevent this substance from completely stopping up the furnace it was found necessary to bore lateral holes through the graphite tube in the hottest zone, at which condensation could not take place. The composition of the substance condensed in the cooler part of the furnace was not determined, although tests indicated that it was not a carbide. Treated with acid, hydrogen sulphide was always evolved showing that impurities from without the furnace proper, probably in the coke, must have diffused through the graphite to the oxide within. The graphite rods were tested and found to be very pure, having been especially prepared for this work through the kindness of the Acheson Graphite Co., of Niagara Falls.

As it was found that rods of magnesia of the desired size could not be obtained by the method above described (at least when carried out on the scale feasible at the time), it was thought that an arc furnace might be more effective. A hollow rectangular graphite boat, 10 × 4 × 4 cm., was used as a receptacle for the fused oxide.

Over the center of this was arranged a powerful alternating current arc into which the oxide was fed from above. The whole was enclosed in graphite bricks, around which were built up fire bricks. In this way irregular masses of the fused oxide, as large as one's hand, were obtained; and from such masses, rods or pieces of the desired size were bored by means of carborundum. The large masses thus obtained were not, however, homogeneous. Certain portions or layers were composed of very fine compact crystals resembling marble, other portions were composed of larger crystals. Some excellent samples were obtained, however, so hard and compact that they were quite non-porous to water and to fused salts. The great difficulty experienced was in getting pieces sufficiently free from minute bubbles or blow holes. Up to the present time we have been unable to completely eliminate these in pieces larger than two or three cubic centimeters. If the process were to be carried out on a much larger scale and a larger mass of oxide brought to a state of quiet fusion and then cooled, better results could undoubtedly be obtained.

PHYSICAL PROPERTIES.

Appearance. — The fused oxide when pure and uncontaminated with particles of graphite is a pure white, very hard crystalline substance. The fused surface resembles glazed porcelain. Depending upon the rapidity of cooling the crystals appear either very minute and compact, giving the structure the resemblance of marble, or fairly large and compactly arranged in layers. The substance takes on a good polish.

Hardness. — The fused oxide is exceedingly hard. Its hardness was found to be between that of apatite, transparent variety, and feldspar, white cleavable variety, being somewhat nearer the former than the latter.

Specific Gravity. — This was determined by the Archimedes method for a number of selected samples and the following values obtained:

Sample *A*. Mean value of three small cylinders used for expansion experiments (see below).	3.485 at 19° C.
Sample *B*. Mean value of large cylinder 5.5 cm. × 1.2 cm. diam.	3.562 at 20° C.
Sample *C*. Mean value of four small irregular pieces.	3.432 at 20° C.
Mean of *A*, *B*, *C*.	3.493 at 20° C.

The specific gravity of the mineral periclase consisting of crystalline magnesium oxide and a little ferric oxide, of the percentage composition :

MgO	FeO
93.86	5.97
93.38	6.01

is given as 3.674.

Melting Point. — The melting point was determined by putting two or more small fragments of the already fused oxide into a graphite tube resistance furnace, holding the current in the furnace constant, and determining the temperature of that part of the tube where the samples were placed by means of an optical pyrometer. If, after a run, the pieces were found to be fused together, the melting temperature was considered to have been exceeded. Thus by making a number of runs, temperature limits were determined between which the melting point lay.

The furnace consisted of a 11″ graphite tube, 1″ in diameter and bored out to ⅝″ inside diameter. Midway between the ends was a ⅝″ hole, opening laterally into the bore of the tube. The ends of the tube were attached to graphite terminal blocks, 6″ square and 3″ thick. The opening in which the sample to be fused was placed was viewed through a larger hollow graphite tube placed at right angles to the furnace tube. To prevent too rapid oxidation of the furnace the tube was surrounded with fine coke and magnesia powder which was held in place by fire bricks and asbestos. By this arrangement when the furnace was heated the pyrometer could be sighted through the horizontal side tube at the opening in the heating tube and the conditions for "black body" radiation were approximately approached. In this furnace temperatures from 1500° to 2500° could be maintained with currents ranging from 300 to 700 amperes. The desired regulation of the current was obtained by an adjustable rheostat in the field of a 25 kw. low voltage D.C. generator.

The temperatures were measured with a Wanner pyrometer which had been calibrated at the Reichsanstaldt. This pyrometer had a range from 900° C. to 2000° C. which could be increased to 4000° C. by means of an auxiliary smoked glass screen.

The samples whose melting points were determined were frag-

ments of magnesium oxide which had been previously fused. In every measurement the samples were placed near the side opening in the furnace tube, so that they were in line with the pyrometer. By this means the temperature of the graphite tube with which the samples were in contact was the temperature measured.

From the series of measurements made it was found that below 1890° C. the fragments did not fuse together or soften. Above 1940° C. they always fused together. This indicates that the melting point of magnesium oxide (fused) is between 1890° C. and 1940° C. In round numbers 1910° C. may therefore be taken as the approximate melting point of the oxide.[1]

Electrical Conductivity. — The electrical conductivity of the fused oxide was determined as follows:

A small cylinder, 8 mm. thick by 14 mm. in diameter, was first prepared by very carefully grinding its surface. This was placed between two pieces of thin platinum foil (*A*) which were pressed against the sample (*B*) by graphite rods (*C*). These were held in an iron frame as shown in Fig. 1. The upper graphite rod was insulated at the top by a piece of fused magnesium oxide (*D*) whose resistance was maintained practically infinite by keeping it outside of the furnace and consequently cool. To insure nearly constant pressure on the sample (*B*) during the heating, a lever (*E*) and spring (*F*) were used as shown. The whole arrangement of this apparatus was freely suspended from an insulated stand in a vertical cylindrical electric furnace of the platinum resistance type. The 110- or 220-volt circuit was connected to the graphite rods (*C*) by means of platinum leads.

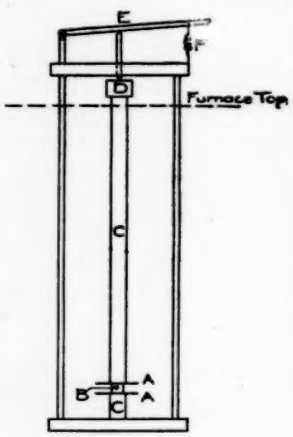

Fig. 1.

The sample to be tested and the graphite rods were connected in series with a Weston voltameter across the 110- (or 220-) volt D.C.

[1] We hope shortly to fix the melting point of this and a number of other refractory oxides with a higher degree of precision than here attempted.

mains. The resistance under investigation being very much greater than the resistance of the voltameter itself (15,800 ohms), the latter could be used as an ammeter and deflections for a constant applied voltage assumed proportional to the current. Hence, if

R = resistance of sample,
R_v = resistance of voltameter = 15,800 ohms,
V = reading with voltameter alone in circuit, *i. e.*, the voltage across mains,
v = reading with voltameter + magnesia sample in series,

then

$$R = \frac{R_v(V - v)}{v}.$$

The temperature was measured by a thermoelectric junction, (platinum, platinum-rhodium), which was calibrated at the sulphur, aluminum, and gold points.

The values of the specific conductivity of the magnesium oxide in reciprocal ohms at various temperatures are given in Table I. and on the accompanying plot, Fig. 2. These values should be considered as maximum values, as slight traces of graphite remained in the sample in spite of the fact that it was heated repeatedly to near its melting point.

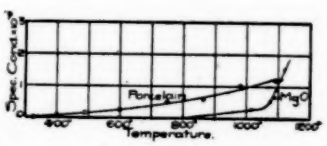

Fig. 2.

For comparison, the conductance of samples of Berlin and Meissen porcelain (glazed) were also measured in the above apparatus, and the values obtained are given in Table II. and on the same plot. The results show that magnesium oxide is a much better insulator than porcelain at temperatures below 1100° C. Above that temperature the large temperature coefficient of the oxide indicates that its conductivity probably becomes greater than that of porcelain.

Our measurements, which were made with direct currents, indicated distinct polarization in the case of porcelain but with the oxide no trace of such action was evident.

TABLE I.

SPECIFIC CONDUCTIVITY OF FUSED MAGNESIUM OXIDE.

Temperature.	Specific Conductivity.	Temperature.	Specific Conductivity.
700° C.		1050° C.	0.34×10^{-6}
800	0.01×10^{-6}	1100	1.00 "
900	0.10 "	1150	2.60 "
1000	0.20 "	[1500[1]	$85. \times 10^{-6}$]

TABLE II.

SPECIFIC CONDUCTIVITY OF PORCELAIN.

Observed Values.			Values by:	
Temp.	Berlin.	Meissen.	Foussereau.[2]	Nernst,[3] Reynolds.
50° C.			0.465×10^{-15}	
200			0.746×10^{-10}	
400	0.05×10^{-6}	0.05×10^{-6}		
500	0.20 "	0.10 "		
600	0.32 "	0.18 "		
700	0.43 "	0.24 "		
800	0.55 "	0.40 "		
900	0.75 "	0.70 "		
1000	1.00 "	0.94 "		3×10^{-5}
1100	1.30 "	1.27 "		

Coefficient of Expansion. — This was determined by Mr. G. W. Eastman[4] by the Fizeau method, using the latest form of Abbé-Fizeau dilatometer, manufactured by the Zeiss Optical Co., of Jena. The interference apparatus was similar to that used by Reimedes, and consisted of two quartz plates, *A* and *B*, cut perpendicular to the optic axis. The samples of fused magnesium oxide used consisted of three small carefully ground cylinders, *D*, 7.4 mm. long and 2.5 mm. in diameter, which served to support the upper quartz plate upon the lower as shown in Fig. 3. These supports were placed at the vertices of an equilateral triangle. The interference fringes were produced between the upper surface of *B* and under surface of *A*. The coefficient of expansion of *D* could be at once computed

[1] Nernst and Reynolds, Landolt and Börnstein's Tables.

[2] Landolt and Börnstein.

[3] Landolt and Börnstein.

[4] Thesis Mass. Inst. of Technology, 1904.

from the measured shift of the fringes due to a measured change in temperature.

The heater consisted of a massive casting of copper so bored that the interference apparatus could be placed at the center and observed by means of a total reflecting prism from the outside side. The temperatures were measured by a very carefully calibrated platinum resistance thermometer, and extended over a range from 120° C to 270° C.

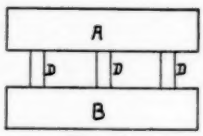

Fig. 3.

The value for the linear coefficient of expansion over this range of temperature was found to be

$$\alpha_t = 10^{-8}[1{,}140 + 0.92(t - 120°)].$$

This value is not much greater than that for quartz crystal cut parallel to its optic axis and is nearly equal to that of platinum, as will be seen by comparison with the following data:

Quartz Crystal.

Randall,[1] $\alpha_t = 10^{-8}[717.0 + 1.620t]$ for temperatures to 250° C.

$\alpha_t = 10^{-8}[1{,}125.0 + 165(t - 250) + 0.00566 (t - 250)^2 + 0.0000134(t - 250)^3]$ for $t = 250°$ to $t = 470°$.

Reimerdes,[2] $\alpha_t = 10^{-8}[692.5 + 1.689t]$ for $t = 5°$ to $t = 220°$.

Eastman,[3] $\alpha_t = 10^{-8}[698.7 + 1.580t]$ for $t = 85°$ to $t = 235°$.

Fused Quartz.

Holborn & Henning,[4] $\alpha = 54.0 \times 10^{-8}$ for $t = 0°$ to $t = 1000°$.

Platinum.

Holborn & Day,[5] $\alpha = (8{,}889 + 1.274t)10^{-9}$ for $t = 0°$ to $t = 1000°$.

Le Chatelier,[6] $\alpha = 1130 \times 10^{-8}$ for $t = 0°$ to $t = 1000°$.

[1] PHYSICAL REVIEW, *20*, 10, 1905.
[2] Inaug. Diss., Jena, 1896.
[3] Thesis Mass. Inst. Tech., 1904.
[4] Ann. der Phys., *4*, 446, 1903.
[5] Ann. der Phys., *2*, 508, 1900.
[6] Landolt & Börnstein's Tables.

The close agreement between the value of the expansion coefficient of fused magnesia and that of platinum should prove a valuable property in the construction of apparatus involving joints of these two materials. We have found in fact that platinum caps ground to fit the ends of rods of the fused oxide remain tight over wide ranges of temperature.

Heat Conductivity. — The heat conductivity has not been determined in this laboratory. In a recent table of thermal conductivities of refractory materials published by Messrs. Hutton & Beard,[1] however, "Magnesia (fused)" is included, the conductivity of this material in the form of granular powder (600 meshes per sq. cm.) being given as $K = 0.00047$ as compared with $K = 0.00029$ for lime, and $K = 0.00028$ for fire brick. No details regarding the preparation of the magnesia are given by the authors.

Chemical Properties. — Fused magnesium oxide possesses in a remarkable degree the ability to withstand chemical action of many neutral salts at high temperatures, and is therefore well adapted for use as vessels and apparatus for containing such salts when subjected to high temperatures. Qualitative tests of the chemical action of various fused salts on the oxide gave the following results.

Silver, sodium and potassium nitrates, sodium and potassium chlorides, bromides and sulphates, zinc chloride and barium nitrate showed no action on a polished sample of the fused oxide when the latter was heated for an hour or more in the fused salt. Barium chloride had a very slight action; sodium carbonate, potassium sodium carbonate, potassium hydrate and cryolite attacked the fused oxide energetically.

Dilute hydrochloric, nitric and sulphuric acids attack the fused oxide in the cold slowly. Concentrated acids are less active than dilute acids.

Electrochemical Laboratory,
Massachusetts Institute of Technology.

[1] Proceedings of the Faraday Society, I., 266, 1905.

DISTRIBUTIONS OF COLLOIDAL NUCLEI AND OF IONS IN DUST-FREE CARBON DIOXIDE AND IN COAL GAS.

By C. Barus.

1. *Apparatus.* — The following experiments were made with the apparatus used in my last experiments[1] with dust-free air. The conveyance tubes between the exhaustion chamber (5 feet long and 1 foot in diameter) and the condensation chamber (18 inches long and 5 inches in diameter) were about 18 inches long and 2 inches in diameter. The rapid exhaustion thus secured is effective, but may not have reached a limit;[2] there is still too much resistance in the connecting pipes. The data obtained with such an apparatus are comparable with each other, and nothing further than this is aimed at, since in view of the very high exhaustions needed the constants for the computations of the absolute nucleations would in any case be lacking. It is a matter of convenience however, to compute the data at the high exhaustion as if the conditions met with at the low exhaustion were indefinitely applicable, and this is the meaning to be given to n, the number of nuclei per cubic centimeter, in the present paper. Moreover n refers to the nucleation left in the *exhausted* fog chamber, supposing that the nuclei are restored to the gas faster than they can be withdrawn by exhaustion or that the nucleation encountered is fixed for any definite environment. Otherwise n (to be multiplied by the volume expansion) would be very much larger.

[1] Physical Review, XXII., pp. 105 et seq., 1906.

[2] The δp in the text is the value observed under isothermal conditions at the fog chamber, the latter being isolated at once after exhaustion from the vacuum chamber. It will be shown elsewhere that this is much too high and that the true δp must be computed from the initial pressures in fog and vacuum chambers and their common pressure when in communication, all at the same temperature. It is then found that a limit of efficiency has in fact been reached and is not inferior to any other apparatus.

The carbon-dioxide used was generated from calc-spar and hydrochloric acid. The gas was eventually passed through a solution of sodic hydro-carbonate, a long tube of dry bicarbonate of soda, a solution of silver nitrate and a calcium chloride drying tube. Then it entered a filter (two feet long) from which it was conveyed very slowly into the fog chamber.

Coal gas taken from a gas pipe was treated in the same way.

2. *Data for Carbon Dioxide.* — In the chart δp shows the drop of pressure on exhaustion, the nucleation being obtained from $s/30$ (approximately) the angular diameters of the coronas, when the eye is at 30 cm. in front, and the source of light 250 cm. behind the fog chamber. The meaning of the other data is obvious, n being the nucleation.

In the early parts of the work the exhaustion δp was usually kept constant with the object of observing the behavior of the mixture of gases beginning with air and terminating with CO_2. About 8 exhaustions were found to lead to the steady behavior of the latter gas. Inasmuch as the original air was still present to the extent of about one per cent. and admixture of this amount may be regarded as inappreciable. In the succeeding parts of the experiments even 4 exhaustions, reducing the air content to but eleven per cent., nevertheless brought out the behavior of CO_2. Moreover, on readmitting air, two exhaustions nearly suffice to restore the air corona. Coronas for a given mixture are definite, being reproduced after several hours.

The relatively small coronas obtained with CO_2 as compared with air for the same drop in pressure and in the same apparatus, gave rise to a suspicion that water nuclei associated with HCl gas might be involved. In special experiments, therefore, atmospheric air was bubbled through HCl and the gas then passed through the same drying train. After three exhaustions exceptionally high air coronas were obtained, showing that the method of producing the gas is here of no consequence, thorough washing presupposed.

The chart gives a sufficient exhibit of the experiments with non-energized CO_2. The gas was then ionized by the X-rays, with the bulb at a distance of 200 cm., and the experiments continued in the same way. The usual constancy of corona at high exhaustions

was observed. The fog limit again lies in a region of exceptionally high exhaustion as compared with air.

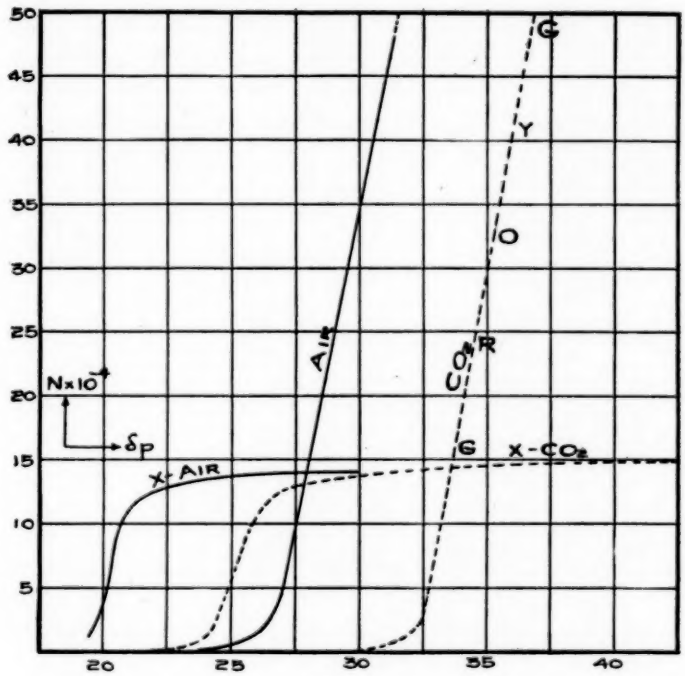

Fig. 1.

3. *The Behavior of Carbon Dioxide.* — The graphs are given in connection with the corresponding earlier data for air, both for the non-energized and the energized state. In both cases the curves are essentially similar in their contours, but the CO_2 curves require much higher exhaustion (δp), throughout, than the air curves. In other words the same coronas occur in CO_2 as in air, provided that in the former gas all the pressure differences are chosen to about 5 to $5\frac{1}{2}$ cm. higher than in the case of air. Similar relations hold for the fog limits as was found directly by Wilson[1] in a small apparatus.

[1] C. T. R. Wilson, Phil. Trans. Royal Soc., volume 189, page 288, etc., 1897. Wilson's fog limits are smaller than suggested above because of his apparently more efficient apparatus. They would agree with those of the text if δp in the latter case were computed as already specified.

The peculiar feature of these results is the degree of parallelism of the CO_2 and air lines both for the non-energized and to a somewhat smaller extent for the energized state. The representative nuclei lie on curves of the same slope. Clearly the phenomena in both cases are alike in character though lying far apart on the chart.

4. *Cause of Differences.* — In view of the more coercible character of CO_2, one would naturally expect larger colloidal nuclei than in the case of air, and it was with this anticipation that the data were investigated. Taken at their full value, however, they would point to a conclusion exactly the reverse of this. The colloidal nuclei in CO_2 are apparently smaller than in the air, and the same is true, caet. par., for the ions.

Unfortunately the precise meaning of these results is not clear: for in the first place the amount of adiabatic cooling may be written in the usual notation,

$$\log \tau_0/\tau = (\gamma - 1)/\gamma \cdot \log p_0/p,$$

and thus between two fixed pressures

$$\log \tau_0/\tau = \text{const.}\ (\gamma - 1)/\gamma.$$

The value of this fraction is for air, .29; for CO_2, .22; for coal gas, .19. In other words the amount of cooling is less in CO_2 than in air under like conditions and hence the reduced efficiency of the fog chamber in the former case is qualitatively compatible with the thermal properties of CO_2 gas.

Quantitatively, however, this compensation does not seem to be sufficient. For instance, the same corona is obtained in air and CO_2 when the pressure difference is 28 cm. and 33.5 cm. respectively. For *like nuclei* this would imply the same degree of supersaturation. Hence if p_1 and p_2 be the vapor pressures of water before (20° C.) and after exhaustion, and $p = 76$ and $p - \delta p$ be the corresponding pressures, the occurrence of like supersaturation implies that

$$\frac{p_1}{p_2}\left(\frac{p - p_2 - \delta p}{p - p_1}\right)^{\gamma} = \frac{p_1}{p_2}\left(\frac{p - p_2 - \delta p'}{p - p_1}\right)^{\gamma'},$$

where p' and γ' refer to CO_2 and where γ is the heat ratio for air.

Hence

$$\frac{\gamma}{\gamma'} = \frac{\log\,(1-(\delta p'+p_2)/p)-\log\,(1-p_1/p)}{\log\,(1-(\delta p+p_2)/p)-\log\,(1-p_1/p)},$$

where the value for $\gamma/\gamma' = 1.10$ as derived for direct experiment.

To compute the value of the same ratio from the coronal experiment it is necessary to know p_2, the vapor pressure on exhaustion and before condensation ensues. This datum is unavailable; but it must be greater than zero and less than would correspond to the decidedly lower exhaustion, $\delta p = 17$ cm., than the one applied ($\delta p = 28$ cm.). Hence limits of the value of γ/γ' may be computed by inserting $p_2 = 0$ and $p_2 = .2$ respectively. The results are $\gamma/\gamma' = .128$ both for the superior and inferior limits, as would be otherwise anticipated.

One may summarize these results as follows. Either the heat ratio of carbonic acid, γ', decreases in comparison with that of air, γ, very rapidly as temperature decreases, so that an average value of $\gamma/\gamma' = 1.3$ instead of $\gamma/\gamma' = 1.1$ is to be used in the preceding experiments; or all the colloidal nuclei in CO_2 though distributed in a way closely recalling that of air, are throughout smaller; at least there is no evidence showing that the colloidal nuclei of a coercible gas like CO_2 are larger than the colloidal nuclei of air. The adequacy of the first hypothesis is improbable since the same γ/γ' would hold for ionized nuclei and for colloidal nuclei, though the phenomena appear in widely different regions of exhaustion. Similarly no suggestion would be offered for the close parallelism of the air and the CO_2 curves throughout their extent. Finally the phenomenon should be accentuated for coal gas where $(\gamma-1)/\gamma$ is smaller, but this is not the case.

5. *Data for Coal Gas.*—These were investigated in the same way as in the preceding case both for the non-energized and for the energized gas, when the X-ray bulb was at a distance of 200 cm. from the fog chamber. The measurements were much less satisfactory than the above, the corona being thin and blurred. As in case of CO_2 the data for coal gas throughout lie in a region of relatively low pressure, *i. e.*, large sudden reductions of pressure are needed to produce the coronas. Fog limits are correspondingly high—

all of which is again qualitively in keeping with the low heat ratio, γ'.

Apart from this the new results with the hydro-carbon gas in the earlier experiments differed thoroughly from the character of the results for air and CO_2. In the non-energized gas the nucleations rose with the pressure difference at a rapidly accelerated rate and this continued to the highest values of δp applied, and long after the air and CO_2 nucleations had become stationary in the given apparatus.

Similarly for the weakly energized gas, the increase of nucleation was very gradual and the asymptote was scarcely reached within the interval, $\delta p = 40$ cm., of the experiment. All this was sharply in contrast with the rapidity with which air and CO_2 approach their respective asymptotes as may be seen by inspecting the chart.

In the final experiments, however, where care was taken to have the exhaustion chamber as well as the fog chamber full of dust-free coal gas, the behavior both for the highly energized and the non-energized states approached that of the other gases in character. The non-energized curves lay between those for air and CO_2, and in the energized gas the highest nucleations were producible.

BROWN UNIVERSITY,
PROVIDENCE, R. I.

STUDIES IN LUMINESCENCE.

By Edward L. Nichols and Ernest Merritt.

VII. Further Experiments on the Decay of Phosphorescence in Sidot Blende and Certain Other Substances.

In the two preceding papers of this series[1] experiments were described in which the phosphorescence of Sidot blende was followed by the spectrophotometer for about ten seconds after the cessation of excitation. At the end of this period the intensity of phosphorescence had fallen to about four per cent. of its original value. Although it was possible to see the phosphorescent light in the spectrophotometer for a much longer period than this, the extreme faintness of the field made accurate measurements out of the question. In attempting to determine the law of decay throughout a wider range we have therefore been compelled to abandon the use of the spectrophotometer and to measure the total light.

Measurements of the total intensity do not, in general, afford a satisfactory means of determining the law of decay of phosphorescence, since the phosphorescence spectrum usually contains two or more bands, which decay at different rates. We have already referred to the difficulties that are met with in interpreting the results of such measurements. In the case of Sidot blende the conditions are, however, relatively simple, for the phosphorescence of the green band is so much more prominent, both in duration and in intensity, than that of the violet bands that the presence of the latter does not appreciably affect the total intensity. Measurements of the total phosphorescence of Sidot blende are therefore practically measurements of the intensity of the green band only. If all parts of this band decay at the same rate, measurements of total intensity will give the same results as measurements taken at some particular portion of the band. Our earlier observations have shown that all

[1] Physical Review, Vol. 21, p. 247, 1905; Vol. 22, p. 279, 1906.

parts of the green band of Sidot blende do decay at the same rate for at least ten seconds. It seems not unlikely, therefore, that this equality of rates will be maintained.

Although the present paper deals chiefly with the phosphorescence of Sidot blende the results obtained in the study of several other substances are also included.

EXPERIMENTAL METHOD.

The apparatus used is shown in Fig. 38. The white screen was removed from a Lummer-Brodhun photometer and the Sidot blende screen, *s*, was put in its place, the active surface of the screen being toward the left. The screen was usually excited by a Lummer mercury lamp, *L*, of the "end on" form. In some instances the carbon arc, and in other cases the spectrum of the carbon arc, was used for excitation. The exciting light could be cut off by means of a shutter, *S*, which at the same time made a record on a chronograph. When the mercury lamp was used in excitation a piece of blue glass, *B*, was placed between the lamp and the screen, so that only the violet lines in the spectrum were used.

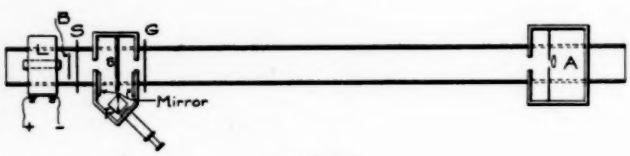

Fig. 38.

The right-hand side of the screen as seen in Fig. 38 was of white paper and could be illuminated by means of the acetylene lamp, *A*. Two pieces of green glass, *G*, served to produce a sufficient color match. The acetylene flame, *A*, was in a metal box, and the light used emerged from a small opening immediately in front of the central part of the flame. Small changes in pressure were therefore without effect upon the intensity of this comparison source.

The procedure in taking observations was as follows:

One observer, with his eyes suitably protected from stray light, watched the decay of the phosphorescence after the shutter had been closed, and recorded by means of a key the instant at which the phosphorescent light and the comparison field were equal. The

second observer then shifted the position of the comparison flame, A, to a slightly greater distance from the photometer, and the time when equality was again reached was recorded as before. In this way it was often possible to get as many as fifteen points on the curve of decay, although a smaller number than this was more usual.

Experiments with Sidot Blende.

In preliminary experiments the light from the carbon arc was used in excitation. It was thought that simpler conditions would be obtained if exciting light having only a small range of wave-lengths was used, and a spectrum of the arc was therefore formed, the violet end of which was used for excitation. The gain in the intensity of phosphorescence which resulted from cutting off the red and infra-red rays was very noticeable.

In our previous experiments with Sidot blende it was found that the decay of phosphorescence during the first seven seconds was in accordance with the law

$$I = \frac{1}{(a + bt)^2},$$

so that upon plotting the curves with T and $I^{-\frac{1}{2}}$ as coördinates a straight line was obtained. Since the distance between the photometer screen and the acetylene flame is proportional to $I^{-\frac{1}{2}}$, it was convenient to plot the results of the present experiments in the same way.

The general character of the decay curves when plotted in this manner is exhibited by the curves of Fig. 39. The violet end of the carbon arc spectrum was used in excitation, and the duration of excitation was varied as indicated.

Inspection of Fig. 39 shows that while each curve starts as a line which is nearly straight in the neighborhood of origin, it soon begins to bend over and ultimately changes into a second straight line having a different slant. This behavior is especially noticeable in the case of long exposures.

If phosphorescence is due to the recombination of ions that have been separated by the action of the exciting light, as assumed in the theory of Wiedemann and Schmidt discussed in our last paper,

it appears that the coefficient of recombination does not remain constant during the whole period of decay. During the first six or seven seconds this coefficient is practically constant, as was shown by the results of our previous experiments. A change then begins which continues for about twenty or thirty seconds, after which the curves indicate a new coefficient, smaller than before. This new coefficient, as is shown by the constant slant of the curves of Fig. 39, remains constant during the rest of the period of decay, or at least until the phosphorescence has become too faint to measure.

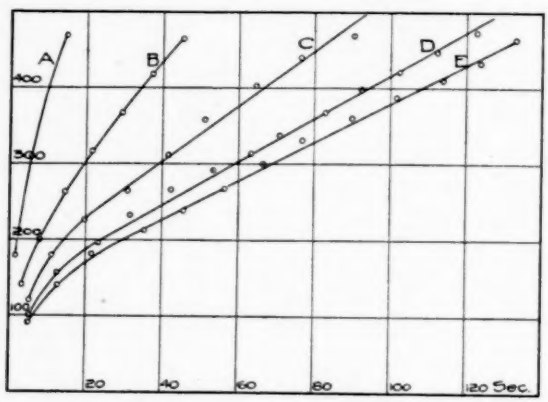

Fig. 39. Effect of duration of excitation. Violet end of carbon-arc spectrum used in excitation. The curves were taken in the order indicated by the letters. The times of excitation were as follows:

Curve *A*, 0.9 sec.
" *B*, 2.4 sec.
" *C*, 4.5 sec.
Curve *D*, 9.2 sec.
" *E*, 17.5 sec.

Whatever theoretical interpretation of the curves is adopted it is clear that the decay of phosphorescence involves two distinct processes which merge into one another. In each of these the decay obeys the simple law already referred to, but the rate at which the phosphorescence dies out is greater in the first process than in the second.

It will be observed that the slant of the curve, for each of the two processes, is a function of the duration of excitation.

In Fig. 40 is shown a series of curves taken under the same conditions as those of Fig. 39, except that the mercury arc was used

in excitation instead of the violet end of the ordinary arc spectrum. One is immediately struck by the difference between the two sets of curves. In Fig. 40 there is a strong tendency toward parallelism in the parts of curves corresponding to the second process. In Fig. 39 no such tendency is observable.

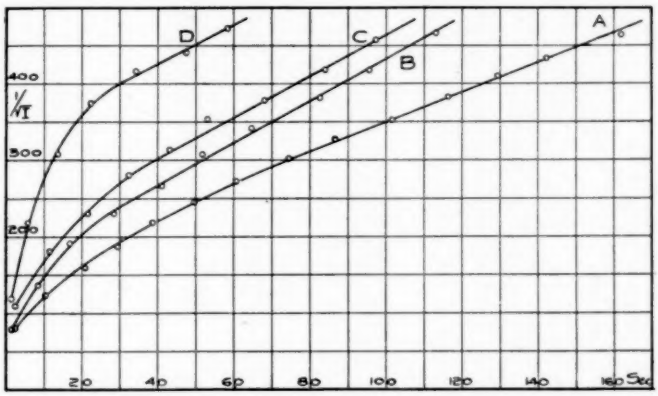

Fig. 40. Effect of duration of excitation. Violet light of mercury arc used for excitation. The curves were taken in the order indicated by the letters. The times of excitation were as follows:

Curve *A*, 27 sec. Curve *C*, 3.1 sec.
" *B*, 10 sec. " *D*, 1.2 sec.

We were at first inclined to ascribe this difference to the fact that different kinds of exciting rays had been used in the two cases. The two sets of curves differ however in another respect, namely, in the order in which the curves were taken. In the first case the curves of short excitation were taken first, while in the latter case the curves corresponding to long excitations were the first observed. It appeared possible that the difference in the form of the curves was due to this difference in sequence rather to the difference in exciting light.

To test this matter the observations plotted in Fig. 41 were made. It will be noticed that the dotted curves are similar to those in Fig. 40 while the full curves are similar to those of Fig. 39. The mercury arc was used in excitation in all cases. But curves taken after the screen had been subjected to the long excitations corresponding to Curves *C* and *D* differ widely from the curves taken with approxi-

mately the same excitation previous to *C* and *D*. A comparison of Curves *A* and *E* illustrates this point, the duration of exposure being exactly the same in each of these two cases.

These results indicate that some change is produced in the phosphorescent material by the action of the exciting light, and that this changed condition persists for a considerable period after all visible phosphorescence has ceased. In other words the effect of a given excitation in producing phosphorescence depends upon the previous history of the phosphorescent substance.

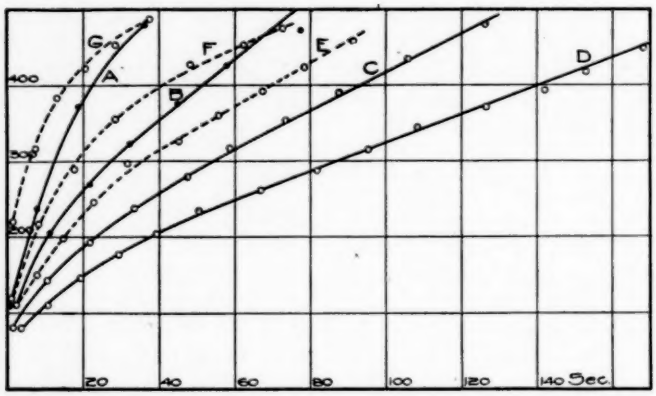

Fig. 41. Effect of duration of excitation. Mercury arc. The curves were taken in the order indicated by the letters. The times of excitation were as follows:

Curve *A*, 4.3 sec.
" *B*, 8.2 sec.
" *C*, 16.0 sec.
" *D*, 56.0 sec.
Curve *E*, 4.3 sec.
" *F*, 1.4 sec.
" *G*, 1.0 sec.

If the screen is allowed to rest in the dark for a number of hours this semi-permanent effect of exposure in part dies out. But rest alone dose not restore the screen completely, even if continued for several days. The effect of rest was also found to be somewhat uncertain, being much greater on some occasions than on others.

Several methods of restoring the screen to a standard condition were tried. Heating the screen to the temperature of boiling water for several minutes and then cooling it again to the temperature of the room seemed effective. But this method required considerable time and has not been thoroughly tested. Cooling the screen to

the temperature of liquid air and afterwards warming it gradually to the original temperature seemed to be without effect.

The well known effect of the red and infra-red rays in suppressing the long time phosphorescence of various substances led us to think that these rays might also prove effective as a means of restoring the screen to a standard condition. This conjecture proved to be correct, and exposure to the red and infra-red rays of a 50 c. p. lamp at a distance of about 20 cm. was found to be both convenient and satisfactory. A piece of ruby glass placed in front of the lamp served to remove the more refrangible rays. An exposure of a few seconds to the rays that passed through the ruby glass was sufficient to bring the screen into what seemed to be a definite standard condition. A longer exposure was, however, ordinarily used.

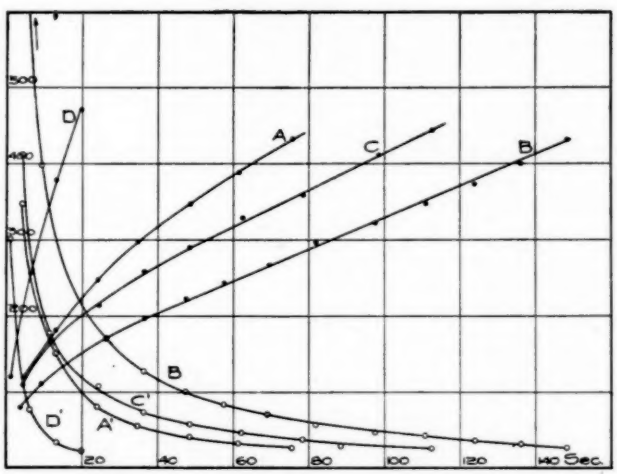

Fig. 42. Illustrating the relative effect of rest and of exposure to infra-red.
A, 10 sec. excitation after rest of 24 hours in the dark.
B, 2 min. excitation.
C, 10 sec. excitation immediately after *B*.
D, 10 sec. excitation after exposure of 4 min. to infra-red from 50 candle power lamp.
Curves *A'*, *B'*, *C'*, *D'* correspond to *A*, *B*, *C*, *D* except that I is plotted in place $I^{-\frac{1}{2}}$.

The change produced by excitation and the effect of the red and infra-red rays are illustrated by the curves shown in Fig. 42. Curve *A* shows the behavior of the screen when exposed for ten

seconds after resting in the dark for twenty-four hours. Curve B is that corresponding to an exposure of two minutes; Curve C was taken with an exposure of ten seconds immediately after Curve B; and Curve D, also with an exposure of ten seconds, was taken after the screen had been exposed to the red and infra-red rays for four minutes.[1]

In some respects the behavior of the screen is analogous to the magnetic behavior of iron. When iron is magnetized a certain residual magnetization remains after the removal of the magnetizing force, and the effect produced by a subsequent magnetizing force depends upon the magnetic history of the specimen. Similarly some change is produced in Sidot blende by excitation which does not immediately disappear upon the removal of the exciting light, and which modifies the effect produced by subsequent excitation.

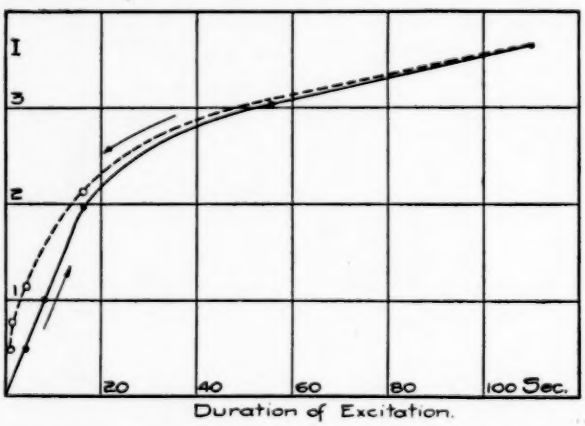

Fig. 43. Hysteresis loop. Ordinates give the intensity of phosphorescence 30 sec. after the end of excitation. The curves from which these points were determined were observed in the order indicated by the arrows.

The analogy is rendered more striking if this property of Sidot blende is exhibited in a different manner, as in Fig. 43. In the curve plotted in this figure the abscissa of each point shows the duration of excitation, while the ordinate gives the corresponding intensity of phosphorescence after thirty seconds decay. The resemblance of the curve to a hysteresis loop for iron is striking.

[1]Experiments dealing with the effect of the infra-red rays during and after excitation will form the subject of a separate paper.

It seems possible that the action of these rays in destroying the residual effect in the phosphorescent substance is similiar to the effect of jarring or tapping in destroying the residual magnetism of a bar of iron. Ignorance of the existence of hysteresis would evidently lead to confusing results in the case of either of these two classes of phenomena. Our delay in recognizing the effect of previous history has in fact made it necessary for us to discard all of our earlier observations.

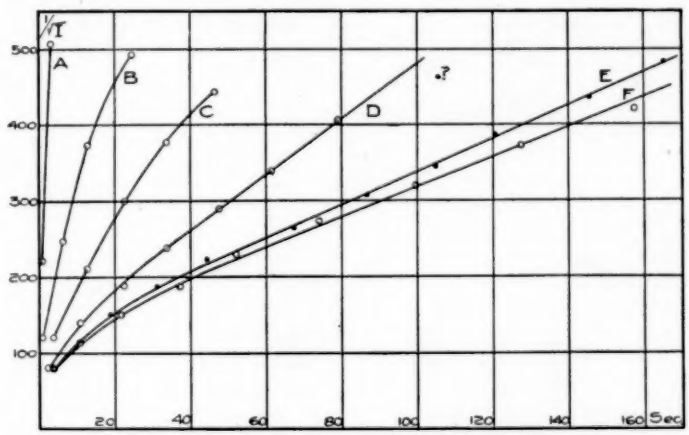

Fig. 44. Effect of duration of excitation. Violet of mercury arc used for excitation. Screen exposed to infra-red for 1 min. before each curve. The times of excitation were as follows:

Curve *A*, 1.2 sec.	Curve *D*, 37 sec.
" *B*, 5.4 sec.	" *E*, 60 sec.
" *C*, 12.0 sec.	" *F*, 15 min.

In our later work the screen was exposed to the red and infra-red rays as described for one minute before each exposure. With this precaution to avoid the effects of hysteresis the curves shown in Fig. 44 were taken to determine the effect of varying times of exposure.

Since our previous experiments have shown that the curves are accurately straight in the neighborhood of $t = 0$, it is possible to determine the initial intensity of phosphorescence by prolonging the curves in each case until they strike the vertical axis. From the intercept thus determined, which is equal to $I_0^{-\frac{1}{2}}$, the initial intensity

can be computed. From the results obtained in this way from the data shown in Fig. 44, Curve *A* in Figs. 45 and 46 has been plotted. In these two figures *I* has been plotted instead of $I^{-\frac{1}{4}}$.

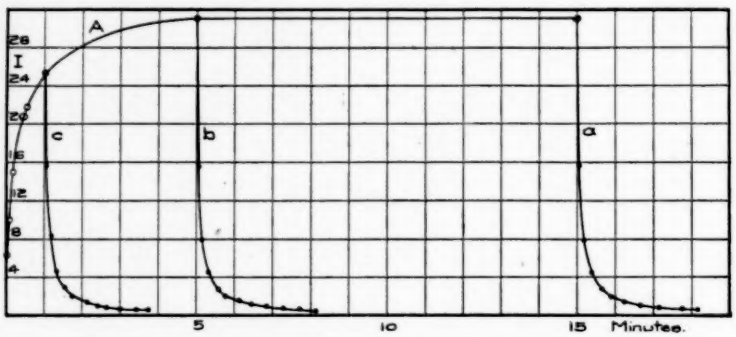

Fig. 45. Effect of duration of excitation. Curve *A* shows the initial intensity of phosphorescence (*I*) as a function of the time of excitation. Curves *a*, *b* and *c* show the decay of phosphorescence after excitations of 15 min., 5 min. and 1 min., respectively.

It will be noticed that the intensity of phosphorescence at first increases rapidly with increased duration of exposure, but that after an exposure of two or three minutes is reached there is little further change. The phosphorescence may be said to be saturated so far as the effect of duration of excitation is concerned. Not only is the initial intensity unaltered by longer excitation, but the form of the decay curve also remains constant, as is indicated by Curves *a* and *b* in Fig. 45. (These curves correspond to Curves *F* and *E* of Fig. 43.)

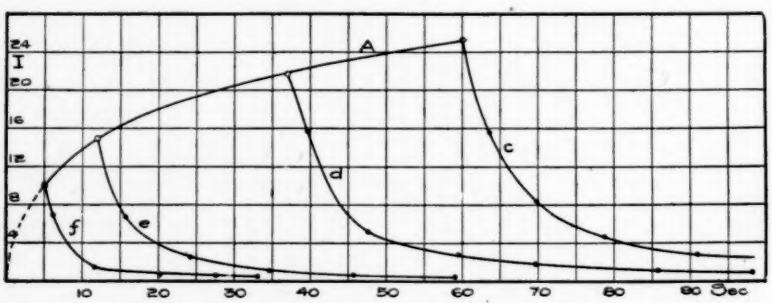

Fig. 46. Effect of duration of excitation. A portion of the same curve shown in Fig. 45 plotted to a larger scale.

We have also studied to some extent the influence of the intensity of the exciting light upon the form of the decay curves. In order

to vary the intensity of the exciting light several metal stops were prepared, which could be placed immediately in front of the mercury lamp. The apertures of these varied from one millimeter in diameter to the full size of the mercury lamp tube, namely, 15 mm. To determine the intensity of the exciting light corresponding to each of these the following photometric method was used: The phosphorescent screen was removed from the photometer and a piece of white cardboard was put in its place. This being illuminated by the violet light from the mercury arc passing through the stop whose constant was to be determined, the intensity was measured by shifting the position of the comparison flame on the opposite side of the photometer. Suitable glass screens were used to equalize the colors on the two sides. To avoid errors resulting from the flickering of the mercury arc ten settings were made for each determination.

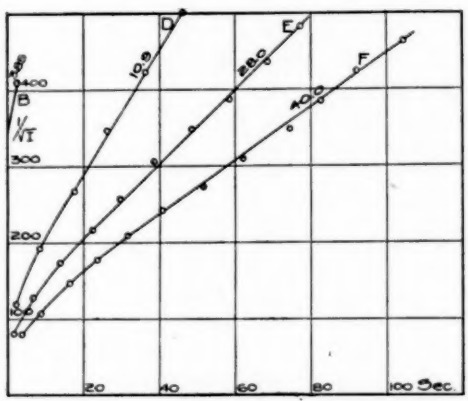

Fig. 47. Effect of varying the intensity of the exciting light. Exposure in each case 20 sec. The relative intensity of the exciting light is marked on each curve.

In Fig. 47 decay curves are shown for different intensities of the exciting light, the excitation in each case lasting for twenty seconds. In Figs. 48 and 49 similar sets of curves are shown for which the excitations were respectively 40 seconds and 2 minutes.

A study of these curves shows that there is some approach to intensity saturation; in other words, the intensity of phosphorescence is nearly proportional to the intensity of the exciting light for small values of the latter, but increases less rapidly than the exci-

tation when the exciting light is strong. This point is well brought out by Curve A in Fig. 50, in which the ordinates are proportional to the initial intensity of phosphorescence, I_0. The values of I_0 were determined from the data of Figs. 47, 48 and 49 by extrapola-

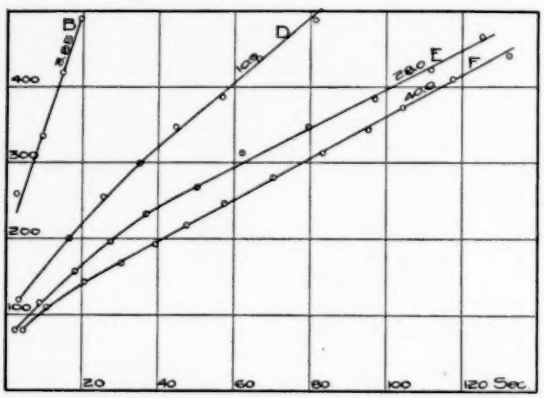

Fig. 48. Effect of varying the intensity of the exciting light (as indicated on each curve). Exposure in each case 40 sec.

tion, upon the assumption that the relation between t and $I^{-\frac{1}{2}}$ is linear for small values of t. Since the early portion of each decay curve is chiefly determined by the first two or three points, which are the most difficult to observe, the values plotted for I_0 are subject to considerable error. Curve A is nevertheless reasonably

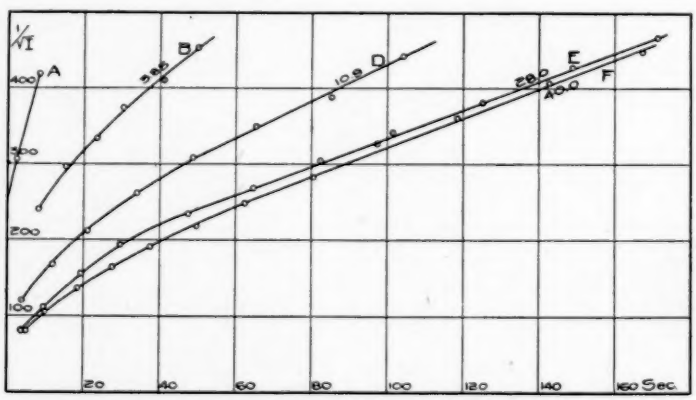

Fig. 49. Effect of varying the intensity of the exciting light (as indicated on each curve). Exposure 2 min. in each case.

smooth and indicates nearly exact proportionality between intensity of excitation and initial phosphorescence. It is only with the most intense excitation used that saturation begins.

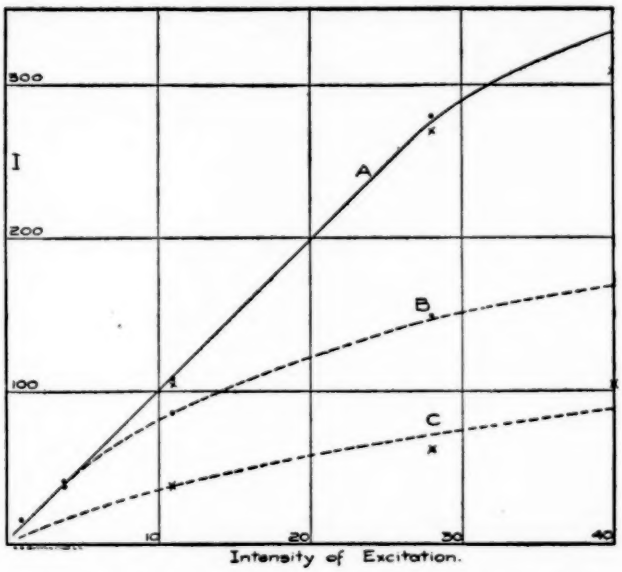

Fig. 50. Curve *A*. Effect of the intensity of the excitation upon the initial intensity of phosphorescence. The points marked by dots are for an exposure of 2 min.; those indicated by crosses are for an exposure of 20 sec. In Curves *B* and *C* the ordinates show the intensity of phosphorescence 1 min. after excitation had ceased.

It is to be observed that in most cases the values of I_0 that are computed from the data of Fig. 47 lie on the same curve as those obtained from the data of Fig. 49. A well-marked difference is noticeable only in the case of the points corresponding to intense excitation. In other words, for weak excitations the intensity of the initial phosphorescence is the same after an exposure of 20 seconds as for one of two minutes. There at first appears to be a contradiction here to the results shown in Figs. 45 and 46. But while this may be due to the uncertainty in the values of I_0, it is readily explained upon the assumption that a weak excitation produces its full effect more promptly. The form of the curves shown in Figs. 45 and 46 is probably largely dependent upon the intensity of the exciting light.

The ordinates of Curves *B* and *C* (Fig. 50) show the intensity of phosphorescence one minute after the exciting light was cut off. For Curve *B* the exposure was two minutes, while for Curve *C* the exposure was twenty seconds. The effect of duration of exposure is here well marked.

In the case of exposures lasting for several seconds or more the phenomena are manifestly complicated by the fact that the semi-permanent change, to which we have already referred, is taking place in the active substance during the time of excitation. It seemed probable that the relation between intensity of excitation and intensity of phosphorescence might prove simpler if the duration of excitation was reduced to a minimum. A series of curves was therefore taken with a spark as exciting source. Preliminary trials showed that the most intense excitation was furnished by discharging eight large jars through a spark gap about 2 cm. long with one cadmium terminal. The distance of the spark gap from the screen was varied from about 10 cm. to 35 cm. A single spark at 10 cm. distance gave an excitation approximately equivalent to thirty seconds exposure to the mercury arc.

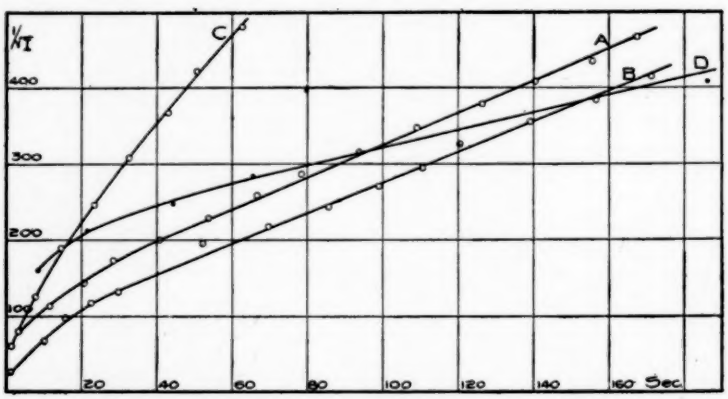

Fig. 51. Typical decay curves for various substances. Curve *A*, Sidot blende; Curve *B*, "Emanations-pulver"; Curve *C*, Willemite; Curve *D*, Balmain's paint.

Experiments with the practically instantaneous excitation produced by a single spark showed that the phosphorescence was proportional to the intensity of excitation, not merely initially but

throughout the whole period of decay. In other words, it was possible to bring a decay curve determined with the spark at a distance d_2 into coincidence with the curve corresponding to the distance d_1 by multiplying each ordinate I_2 by the ratio d_2^2/d_1^2.

Experiments with Different Phosphorescent Substances.

It is natural to inquire whether the complex phenomena exhibited by Sidot blende are peculiar to this particular material, or whether its behavior is typical for a large class of phosphorescent substances. In order to test this matter we have determined the decay curves under similar conditions with three other substances, namely, "Emanations-pulver,"[1] willemite and Balmain's paint. Characteristic curves for these three substances together with a representative curve for Sidot blende are shown together in Fig. 51. It will be noticed that the curves are all of the same type. In each case the decay is at first rapid and apparently according to the same law that was found to hold during the early stages of decay in the case of

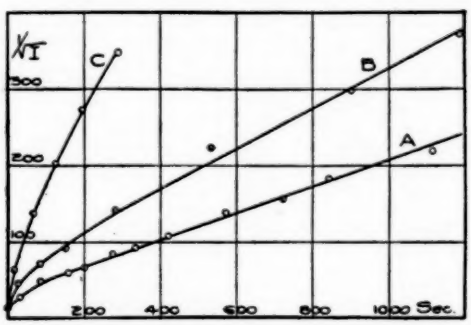

Fig. 52. Decay curves plotted from the data of E. Becquerel. (Ann. de Chimie et de Physique, series 3, Vol. 62, 1861.)

Curve *A*, Sulfure de calcium lumineux vert (2, p. 69).
" *B*, Sulfure de strontium lumineux vert (p. 71).
" *C*, Sulfure jaune-orangé vif (p. 68).

Sidot blende. After twenty or thirty seconds the curves begin to bend, and finally become straight lines whose slant is less than that of the earlier part of the curve.

[1] Obtained from Leppin and Masche, who do not state the composition of the powder. It is said to be especially sensitive to the influence of the radioactive emanations.

Upon plotting the data of E. Becquerel[1] in the same manner we find that in several cases the curves are of exactly the same type as those obtained by us. Three such curves are shown in Fig. 52. In fact all the data recorded by Becquerel in his classic papers on this subject give curves which show the same general characteristics, although in several instances the curves are not so smooth as those shown in this figure.

It is interesting to note also that the data of Darwin[2] on Balmain's paint give a curve similar to those obtained by us with this substance when plotted in the same way. Two decay curves taken by E.

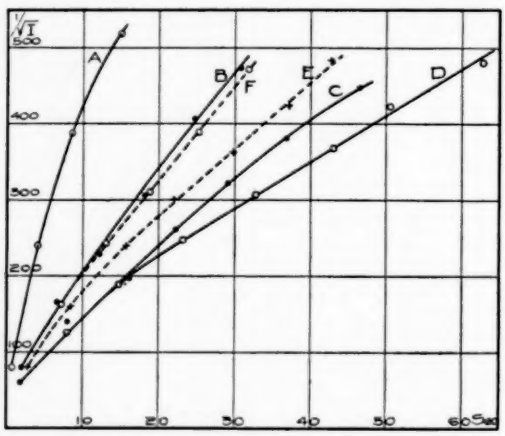

Fig. 53. Willemite. Excited by a spark between iron terminals. The curves were taken in the order indicated by the letters, and with the excitations stated below:

Curve *A*, 0.7 sec.	Curve *D*, 60.0 sec.
" *B*, 3.4 sec.	" *E*, 3.9 sec.
" *C*, 9.0 sec.	" *F*, 1.0 sec.

Wiedemann[3] with Balmain's paint also show the same characteristics.

It appears therefore that the decay curve for Sidot blende is similar in its main features to the curves obtained for a large number of other phosphorescent substances. In fact we do not know of

[1] Becquerel, La Lumière. Also Annales de Chimie et de Physique, Series 3, Vol. 62, 1861.

[2] Darwin, Philosophical Magazine, Vol. 11, p. 209, 1881.

[3] E. Wiedemann, Zur Mechanik der Leuchtens, Wied. Ann., Vol. 37, p. 177 1889.

any case of long time phosphorescence which shows a different type of curve.

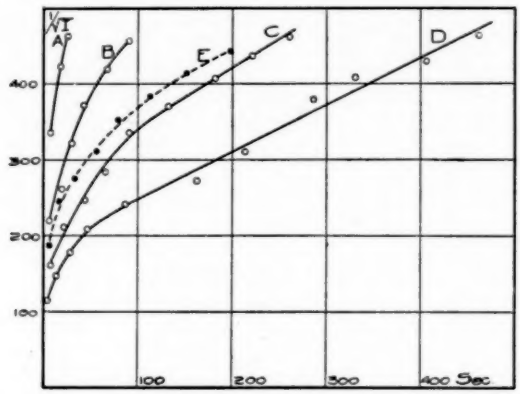

Fig. 54. Balmain's paint. The curves were taken in the order indicated by the letters, and with the following excitations:

Curve *A*, 5.9 sec.
" *B*, 12.0 sec.
" *C*, 26.0 sec.
Curve *D*, 42.0 sec.
" *E*, 6.4 sec.

The peculiar behavior of Sidot blende which we have compared with magnetic hysteresis is also exhibited by willemite and Balmain's paint, as illustrated in Figs. 53 and 54. In each of these cases it is evident that the effect of a given excitation is dependent on the previous history of the substance. We have not yet had an opportunity to test this phenomenon in other substances.

Summary.

The most important points brought out by the experiments here described may be briefly stated as follows:

1. *Form of Decay Curve.* — The curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of t as abscissas is a straight line for small values of t; it changes to a curve concave toward the axis of t as t increases; but for still larger values of t the relation between $I^{-\frac{1}{2}}$ and t is again linear, and remains so until I becomes too small to measure. In other words the decay curve, when plotted in this way, consists of two straight portions which gradually merge into one another.

2. *Effect of Duration and Intensity of Excitation.* — Not only the intensity of phosphorescence, but also the form of the decay curve, is dependent on the intensity and duration of excitation. The slant is altered in each of the straight parts of the curve by changing either of these two factors in the excitation.

3. *Hysteresis.* — The behavior of the phosphorescent substance with a given excitation depends upon its previous history. Some semi-permanent change is produced by excitation which persists for several hours, or even for several days, after visible phosphorescence has ceased.

4. *Effect of Red and Infra-red Rays.* — In the case of Sidot blend the semi-permanent condition produced by excitation may be destroyed and the screen restored to a standard state by brief exposure to the red and infra-red rays. We have not yet determined whether the same effect is produced by the long waves in the case of other phosphorescent substances.

AN INDUCTANCE AND CAPACITY BRIDGE.

By A. de Forest Palmer, Jr.

THE apparatus described herein, was developed, primarily, for the use of students in the Physical Laboratory of Brown University, the idea being to provide easily workable methods by which inductances and capacities can be compared, with an accuracy of about one tenth of one per cent., without the use of elaborate or expensive instruments. While the precision sought is considerably below that desirable in the most exact work, it is amply sufficient for the purpose and, indeed, for most practical work. With the exception of the resistance boxes, condenser and galvanometer, all of the necessary apparatus was built in the laboratory and, though somewhat roughly constructed, it gave results well within the desired limit. A brief description of its essential features is, accordingly, given in the hope that it may be found useful in other laboratories.

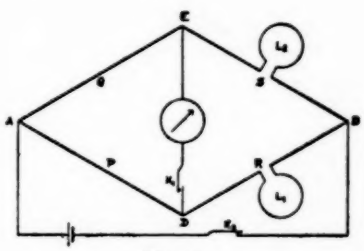

Fig. 1.

Maxwell's[1] method for the comparison of two inductances (L_1 and L_2) is illustrated in Fig. 1. P and Q are noninductive resistances; R represents the resistance of the coil L_1 plus the noninductive resistance in series with it between B and D, and S bears the same relation to B E. When the bridge is in balance for alternating or intermittent currents,

$$\frac{L_1}{L_2} = \frac{P}{Q} \qquad (1)$$

provided the steady current relation

$$PS = QR \qquad (2)$$

[1] Maxwell, "A Treatise on Electricity and Magnetism," third edition, Vol. II., p. 398.

is also fulfilled. Fig. 2 shows Maxwell's[1] arrangement for the comparison of an inductance with a capacity. The letters have the same significance as in Fig. 1 with the addition of C to represent the capacity of the condenser. When the resistances are so chosen that equation (2) is satisfied and the bridge is also in balance for alternating currents

$$L = CQR. \tag{3}$$

Under suitable conditions, these methods are very sensitive but, owing to the necessity of a double adjustment for direct and alternating current, their practical application is somewhat tedious. A further difficulty arises from the fact that few resistance boxes are subdivided sufficiently to permit an exact balance. If the fine adjustment is accomplished with an ordinary slide wire, the battery and galvanometer leads cannot be kept in a fixed position and near together. Furthermore, the connection wires of the bridge will include a considerable area. The error due to the inductances thus introduced would rarely exceed one tenth per cent., but it should be avoided if possible. The tedium of the methods may be considerably reduced by taking P equal to R and Q equal to S so that the bridge is always in balance for steady currents whatever the actual value of these resistances. Balance for alternating current may then be easily attained by altering P and R or Q and S by equal amounts.

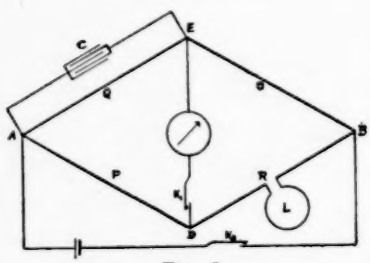

Fig. 2.

The apparatus, designed to carry out these operations and to eliminate, as far as possible, all inductances save those compared, is illustrated, diagrammatically, in Fig. 3. It is, essentially, a connection board provided with a series of brass contact blocks and three double slide wires. The blocks, taken from an old rheostat, are about 1.5 by 2 inches on the top face and .75 of an inch thick. They are bolted securely to a slab of slate and may be connected by large well fitting plugs. Each block is provided with two bind-

[1] Maxwell, l. c., p. 425.

ing screws and a socket for the movable binding posts that terminate the battery and galvanometer leads. The slide wires D, C and D' are somewhat over one meter long and are stretched, parallel to one another, along the top of a wooden meter scale. D and D' are manganin, No. 22 B. S., and are soldered to small brass plates that are securely clamped to adjacent contact blocks by large binding screws. The copper wires C are insulated from D and D', except at the sliding contacts, and may be connected to the galvanometer as indicated at G'. A longitudinal section of the sliders C_1, C_2 and C_3 is exhibited, on a somewhat enlarged scale, at S. These sliders are, essentially, small brass tripods with feet grooved to fit the three wires and they are held firmly in place by inverted U's, of vulcanized fiber, terminating in brass springs that bear against the under side of the wooden scale. The contact pressure is transmitted and regulated by an adjusting screw that passes through the bend of the U and engages the hole H. The resistance of these contacts was found to be very small and surprisingly constant.

Fig. 3 also shows connections arranged for the comparison of two inductances L_1 and L_2. R_1, R_2, R_3 and R_4 are variable non-inductive resistances, of the common plug cutout pattern, guaranteed, by the makers, to be accurate within one tenth per cent. The galvanometer is connected at G and G' and the battery at B and B' through a secohmmeter. In practice, equal resistances are included in R_3 and R_4, plugs are placed at 2 and 6, and balance for steady current is obtained by adjusting R_1, R_2 and X. After removing the plugs from 2 and 6, balance is again produced by altering R_3 and Y. Finally, with the secohmmeter in motion, balance for alternating current is attained by moving the contact C_3 and, if necessary, making equal changes in R_3 and R_4. Unless the resistances in the boxes at R_3 and R_4 are very well adjusted, it will generally be necessary to repeat the two latter operations but in this case, the final adjustment can always be made, with the contacts C_2 and C_3, so that exact balance is observed with either direct or alternating current.

For the comparison of an inductance with a capacity the coil L_2 is removed, plugs are placed at 2 and 6, the condenser is connected

between A and E, and R_3 is made equal to R_4. Balance for direct current is first obtained by altering R_1, R_2 and X. The adjustment with alternating current is then accomplished by making equal variations in R_3 and R_4 and moving the contact C_3. If necessary, these operations are repeated until the bridge is in balance for both types of current, a condition that seldom requires more than two trials.

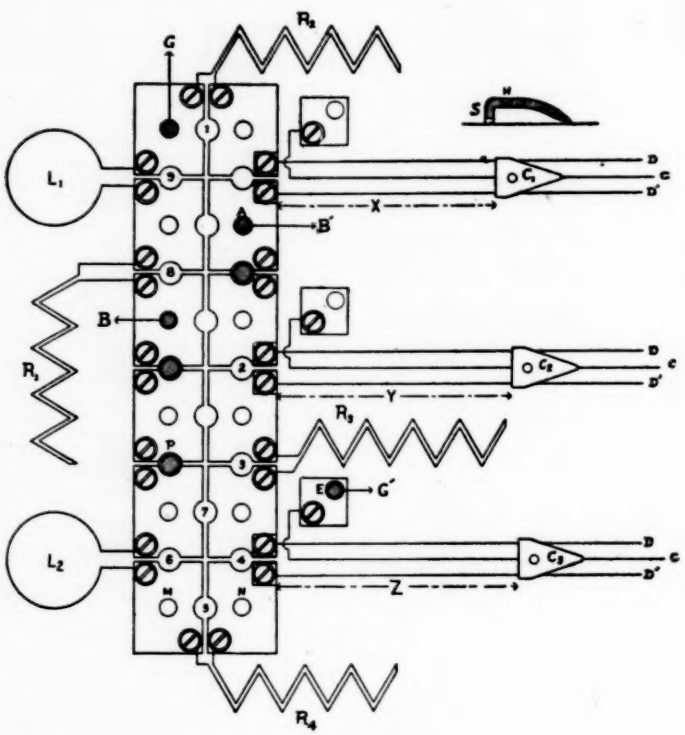

Fig. 3.

When the resistances R_3 and R_4 are so large that a variation of one ohm is within the required limit of accuracy, a plug may be placed at 4 and the condenser connected at N instead of E.

By comparing Fig. 3 with Figs. 1 and 2, it is obvious that

$$P = R_2 + a_1 X \tag{4}$$

and

$$Q = R_3 + a_2 Y + a_3 Z, \tag{5}$$

where X, Y and Z are bridge readings; a_1 is the sum of the resistance per unit length of the manganin wires at X; a_2 bears the same relation to Y; and a_3 is the resistance per unit length of the wire D at Z. Also, in virtue of the adjustments described above, P equals R, Q equals S, and equations (1) and (2), or (2) and (3), are satisfied.

For the purpose of testing the accuracy attainable with the apparatus, three coils (A, B and C) were inter-compared by the first of the above methods and then separately compared with several different capacities by the second method. During these comparisons the sliding contacts were set to an exact balance, but readings were taken to the nearest millimeter, since the error thus introduced was always much less than one tenth of 1 per cent. of either P or Q. Reduction of the observations was facilitated by the use of graphs, constructed with bridge readings as abscissas and corresponding resistance as ordinates. These graphs were drawn to such a scale that the products a_1X, etc., could read off directly with the required degree of precision. This was accomplished, on a sheet of convenient size, by drawing several parallel lines, each representing about 20 centimeters of the wire.

The results of the first series of observations are given in Tables I., II and III. L_A, L_B and L_C represent the inductance of the coils A, B and C, respectively, and the other letters refer to Fig. 1. The values under P and Q were calculated by equations (4) and (5), and those under L_B/L_C, etc., by equation (1). The average deviation of a single observation from the mean is .064 per cent. in Table I., .084 per cent. in Table II., .061 per cent. in Table III.

TABLE I.

L_1	L_2	P	Q	L_B/L_C
C	B	2.102	3.619	1.7217
"	"	3.110	5.361	1.7238
"	"	12.110	20.882	1.7244
"	"	102.083	175.671	1.7210
B	C	4.060	2.357	1.7226
"	"	7.056	4.094	1.7235
"	"	5.102	2.960	1.7236
"	"	6.040	3.500	1.7257
			Mean	1.7233

TABLE II.

L_1	L_2	P	Q	L_A/L_B
B	A	7.074	10.025	1.4171
"	"	13.060	18.518	1.4179
"	"	6.105	8.665	1.4193
"	"	8.021	11.370	1.4176
A	B	5.081	3.574	1.4217
"	"	6.744	4.753	1.4189
"	"	9.865	6.952	1.4194
"	"	13.873	9.764	1.4209
			Mean	1.4191

TABLE III.

L_1	L_2	P	Q	L_A/L_C
A	C	13.978	5.708	2.4489
"	"	7.860	3.212	2.4470
"	"	8.731	3.570	2.4456
"	"	24.105	9.842	2.4492
C	A	4.116	10.057	2.4434
"	"	8.137	19.897	2.4452
"	"	12.113	29.621	2.4454
"	"	6.120	14.974	2.4466
			Mean	2.4464

A comparison of the individual coils with the sections of a mica condenser, by Elliott Bros., is exhibited in Table IV. Column C gives the nominal value of the capacities used. The sub-letters on the P's and Q's indicate the coil connected at L, Fig. 2, or L_1, Fig. 3, during the corresponding observation. The ratios given in the last three columns were each calculated from pairs of observations, tabulated in the same horizontal line, by the equation

$$\frac{L_A}{L_B} = \frac{P_A Q_A}{P_B Q_B}, \tag{6}$$

which follows directly from (3) when P is taken equal to R. The average of the individual deviations from the mean is .032 per cent. of L_A/L_C, .049 per cent. of L_A/L_B, and .070 per cent. of L_B/L_C. Since the actual capacity of the condenser was unknown, it was impossible to determine the exact value of the inductances but an idea of their magnitude was obtained from the observations given in the

first two rows of Table IV. The reduction was made by equation (3), using the nominal value of the capacity. The results were .0161 Henry for coil A, .0113 Henry for coil B, and .00658 Henry for C.

TABLE IV.

C	P_C	Q_C	P_B	Q_B	P_A	Q_A	L_A/L_C	L_A/L_B	L_B/L_C
1.0	3.132	2,103	5.092	2,229	7.062	2,280	2.4446	1.4186	1.7232
1.0	6.137	1,072	7.098	1,597	11.066	1,454	2.4457	1.4195	1.7230
.5	6.139	2,150	13.094	1,737	11.066	2,917	2.4456	1.4193	1.7232
.5	9.137	1,445	17.098	1,329	24.056	1,342	2.4452	1.4207	1.7211
.2′	9.137	3,573	43.093	1,306	24.056	3,320	2.4464	1.4192	1.7239
.2′	16.137	2,022	19.100	2,945	34.064	2,343	2.4460	1.4189	1.7239
.2	16.137	2,040	19.100	2,971	34.064	2,365	2.4472	1.4197	1.7237
.2	12.132	2,714	33.094	1,716	54.051	1,490	2.4460	1.4182	1.7249
.1	22.132	2,986	33.100	3,446	54.067	2,993	2.4487	1.4187	1.7260
.1	42.129	1,570	43.100	2,640	104.048	1,554	2.4447	1.4211	1.7203
						Mean	2.4460	1.4194	1.7233

The observations in Table IV. may also be used, in an obvious modification of equation (3), to calculate the ratio of the capacities given in column C. The ratio of each of the subdivisions to the total capacity of the condenser was thus determined and the results are given in Table V. The first column gives the coil used in making the comparisons and the numbers over the other columns indicate the nominal capacity of the sections. The average deviation of a single observation from the mean does not exeeed .07 per cent. in any of these determinations.

TABLE V.

Coil.	.5	.2′	.2	.1
C	.49902	.20176	.20008	.09967
"	.49830	.20163	.19980	.09946
B	.49904	.20167	.20002	.09952
"	.49885	.20152	.19960	.09962
A	.49880	.20160	.19986	.09948
"	.49850	.20160	.19979	.09952
Mean	.49875	.20163	.19986	.09954

By a slight modification of the connections given in Fig. 3, the apparatus may be adapted for Anderson's[1] method of comparing

[1] Anderson, Phil. Mag., Vol. XXXI., p. 329, 1891.

inductance and capacity illustrated in Fig. 4. For this purpose, the plug at P, Fig. 3, is removed and a noninductive resistance R_5 is connected between the blocks it joined. The coil L_2 is removed, plugs are placed at 2 and 7, the galvanometer terminal G' is removed from E to M, and the condenser is connected between A and

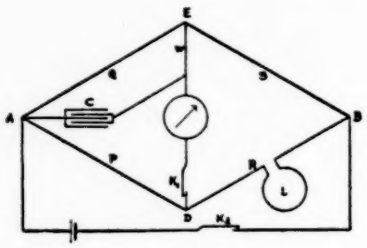

Fig. 4.

M. R_3 is taken equal to R_5 and balance for steady current is obtained by adjusting R_1, R_2 and X. Balance for alternating current is then secured by altering R_4 and Z. After these adjustments, we have on comparing Figs. 3 and 4

$$S = R_5 = R_3 = Q, \tag{7}$$

$$R = P = R_2 + a_1 X, \tag{8}$$

$$W = R_4 + 2a_3 Z, \tag{9}$$

where the significance of the letters is apparent from the figures and the discussion of equations (4) and (5). Hence the inductance L may be determined in terms of the capacity C by the well-known formula

$$L = C\{W(P + R) + PS\}, \tag{10}$$

or, since R is equal to P, by the formula

$$L = CP(2W + S). \tag{11}$$

The foregoing examples are sufficient to show the application of the apparatus in methods depending on the principle of Wheatstone's bridge. The advantages gained by its use arise from the compact arrangement of the connections and the employment of noninductive slide wires. Provided the resistances, included in R_1,

R_2, etc., are properly constructed, the bridge is practically free from inductance except in the coils under comparison. The necessary adjustments can be rapidly and accurately made without changing the relative position of the battery or galvanometer leads. The results, quoted in the above tables, show that inductances and capacities can be compared, by the methods described, with a precision equal to that of the available resistances.

BROWN UNIVERSITY,
April 20, 1906.

AMERICAN PHYSICAL SOCIETY.

DIRECT READING METHODS OF RESISTANCE COMPARISON.

BY F. A. WOLFF.

THE paper contains a description of direct-reading methods employed at the Bureau of Standards for the intercomparison of resistance standards and for the calibration of resistance boxes.

The former are compared by the aid of a shunt compensated ratio set of which one arm is subdivided into four sections each provided with a ten-step shunt dial. The total resistance is thus adjustable in steps of one millionth with a range of one per cent. The principle may be applied to the Wheatstone bridge method and the Kelvin double-bridge method.

For the calibration of resistance boxes a modification of the method of Matthiessen and Hockin is employed, the bridge wire being replaced by a series of equal coils of relatively high resistance so arranged that any desired number may be put in series. By the aid of a Varley switch, any four adjacent coils may be shunted by a circuit of equal resistance including at its middle part a bridge wire corresponding to a range of $\pm$ 1 per cent. The method may be illustrated by the following example: To compare the coils of a box of a given decade, the first coil of the next higher decade and sum of the coils of the next lower decade, they are connected in series and joined in parallel with the calibrating apparatus. The number of steps required is given by the sum of the quotients obtained by dividing the nominal values of the separate coils by their greatest common divisor, thus for a series Σ1, 1, 2, 2, 5, 10, twenty-one are required while if a standard is included twenty-two steps are necessary. Balance readings are taken for each contact block of the box and the differences between adjacent readings give the relative values of the coils intercompared. Connecting resistances in the box are eliminated by taking two readings at their terminals while the resistance of the leads to the calibrating apparatus is eliminated in the usual manner by transferring battery or galvanometer connections.

The method is applicable wherever it is possible to apply a galvanometer contact to the contact blocks between adjacent coils, so long as the balance falls within the range of the bridge wire.

The advantages of the method consist in the elimination of plug and contact resistances, in the employment of only one standard per decade, in furnishing double checks for each decade and in the relative ease and rapidity with which results are obtainable.